QUALITATIVE DETERMINATION

OF

ORGANIC COMPOUNDS

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BY

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PREFACE.

THE following pages contain a systematic presentation of Qualitative Practical Organic Chemistry in a manner somewhat similar to that used in Inorganic Chemistry.

The book has been divided into two parts. The first part is almost purely practical, and contains the Reactions of all the more important *groups of organic substances* in a new systematic form which it is believed will be found very convenient. Here appeal is made more to group reactions of a systematic kind—so far as these can be applied qualitatively—than to the numberless reactions of unknown nature, mostly depending on colour changes, which do duty as "Identification Reactions."

The second part consists of a fairly complete classification of the *main types of Reaction* among Organic Compounds, with suitable examples illustrated by equations. For good reasons it seemed better not to include equations in the first part.

The book is intended for University students, but it will be found useful to anyone requiring help in the Identification of Organic Compounds. This scheme has been used by my own students for some years.

J. W. SHEPHERD.

EXPLANATION OF METHODS OF CLASSIFICATION AND REFERENCE.

THE Reactions of Organic Compounds are of great variety and of many different types. A systematic classification of these Reactions has been made in Part II.: in this classification the main types have been numbered with Roman numerals, sub-sections are indicated by Arabic numerals, and further sub-divisions (according to reagent used, etc.) are indicated by English small letters. Thus each type of reaction has a distinctive reference symbol, such as VII. 3 *b*, indicating its position in the classification of Part II.

Part I. contains a description of the various types of compounds. Here the type or compound is defined by name. Then there follows an account of its physical properties. Then its characteristic chemical reactions are given, with references in each case to the classification in Part II. The typical equations for these chemical reactions are given in Part II. only.

Many of these Reactions are not available as Tests throughout all the various groups to which they apply. For instance, the results may not be characteristic when applied qualitatively, or may require complex methods to make them obvious; yet the reaction may be most important theoretically, or may even be the group reaction—as in the case of the group reaction for OH with phosphorus pentachloride.

Further, the order in which the Reactions available as Tests may be applied in testing unknown substances will differ from that given in Part I. Here they are arranged in the order in which they arise when the various groups are considered in a systematic survey.

There follows, therefore, at the end of Part I. a systematic Scheme of Tests for the identification of unknown substances. In this the main Tests are distinguished by Roman numerals, subsections being indicated by English capitals. References to this Scheme of Tests are always prefixed by the word *Test*, and are thus easily distinguished from references to Part II.

Sections of the book which are of less importance are indicated by an asterisk (*). Experiments which should be performed in a fume chamber are indicated by a dagger (†).

ABBREVIATIONS.

aq. = aqueous or water.
b.p. = boiling point.
c.c. = cubic centimetre.
cm. = centimetre.
conc. = concentrated.
cpd. = compound.
dil. = dilute.
insol. = insoluble.
m.p. = melting point.
O.S. = original substance.
pp. = precipitate.
ppd. = precipitated.
pptn. = precipitation.
s.g. = specific gravity.
sol. = soluble.
soln. = solution.
subst. = substance.
sym. = symmetrical.
t.t. = test-tube.

The meaning of other occasional abbreviations will be obvious from the context.

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CHAPTER I.

ELEMENTARY COMPOSITION.

Organic Chemistry may be defined as the Chemistry of the Carbon Compounds. That this causes the inclusion of many compounds generally considered inorganic may be considered an objection to the definition. But the ordinary place of these compounds in chemical study is merely one of convenience and not of system. For example, in the case of carbon dioxide and the carbonates, there is ample justification for including them in Organic Chemistry; the compounds nearest related to carbonic acid are always considered organic, the acid itself, HO,COOH, being the first member of a homologous series—the hydroxy acids—though like the first members of other series, as H,CH_2OH, H,COOH, it is rather aberrant, from the fact that in it and in these cases, only one group, COOH, CH_2OH, is truly organic. Metallic carbides also in many cases are closely connected with hydrocarbons—into which they pass on treatment with water or acids—so that they might also be considered organic.

Further, this separation of the science into water-tight compartments is now seen to be a mistake, though the great complexity of organic compounds and the fact that the reactions do not have the simplicity of inorganic reactions, *i.e.* are seldom ionic reactions, makes a scheme for the identification of organic compounds by chemical tests, even common ones, rather lengthy and complex.

Of course, the final court of appeal is the result of a quantitative analysis, of combustions for carbon and hydrogen, for halogens, nitrogen, etc., as may be necessary. But obviously this tells little about the kind of compound, and it has to be supplemented by information as to the arrangement in groups of the constituent atoms. This the scheme given later is intended to supply, in a qualitative way.

There has been already a good beginning made with "Proximate Organic Quantitative Analysis," the quantitative determination of organic groups. This will be more complex and possibly less accurate than Quantitative Inorganic Analysis—the determination of ions or ionic groups.

All the known elements, with the usual exception of the Argon group, may take their place in an organic compound, though this place for most of the metals is rather an outside one, viz. as salts of organic acids with the metals. But some metals may enter into closer relations with organic compounds than that merely of the positive ion of a salt; *e.g.* Zn, Hg, Al, etc., in the alkyl and aryl compounds, $Zn(CH_3)_2$, $Hg(C_6H_5)_2$, etc., third group metals in the peculiar complexes with hydroxy (etc.) acids—chromoxalates, ferritartrates, etc., and with sugars (see section on these); while many proteins, etc., naturally contain metals, as iron in haemoglobin of the blood and in chlorophyll of plants; and artificial compounds have been made, containing silver, and sometimes mercury, replacing some part of a natural protein molecule, *e.g.* protargol contains silver. The metal is not separated as a positive ion in solution in these cases.

DETERMINATION OF THE ELEMENTS PRESENT.

If the substance is known to be organic, the application of a test for carbon may seem rather unnecessary, but the simpler test for this purpose gives valuable evidence as to the nature of the compound—in particular as to whether it may or may not belong to the aromatic division, besides giving evidence as to the presence in it of fixed inorganic constituents.

There is no simple qualitative test for oxygen in organic substances, though one might be desirable. As in inorganic substances, oxygen so often forms part of a group, *e.g.* NO_3, nitrate; SO_4, sulphate; OH, hydroxide; SO_3H, sulphonate; NO_2, nitro; which can generally be identified or determined as a whole, that it is not necessary to find oxygen itself.

The vast majority of organic substances contain hydrogen—except metallic oxalates, cyanides, thiocyanates, carbonates, and a few others, so that the determination of its presence seems rather useless; besides for conclusive evidence the substance must be

perfectly dry and contain no "water of crystallisation," and the attainment of certainty on these points is more difficult and troublesome than the test itself.

Ignition Test for Carbon and for Ash.

Heat gradually a small quantity of the substance over a Bunsen flame, on a piece of thin porcelain (a crucible lid or a smaller piece of a larger broken dish), or if reducible metals (those of the first two analytical groups and zinc) are known to be absent, on thin platinum foil.

The platinum foil might be destroyed by alloying with the reducible metal produced on heating its organic compound. A metallic support has the advantage that the higher conductivity of the metal causes a more complete combustion of the mass, so that even a piece of copper foil may be found useful here.

Of course the most direct test for the presence of carbon is the following:—

Mix the substance with copper oxide powder thoroughly. Put into a hard glass t.t. and fill up with granulated copper oxide (Fig. 1). Fit the t.t. with a cork and delivery tube dipping into a quantity, not too small, of limewater in a t.t. Support the t.t. in a horizontal position and heat strongly from the granulated oxide backward along the tube, keeping the front part red hot. The evolution of carbon dioxide, rendering the limewater milky, proves the presence of carbon in any form, even as carbonate.

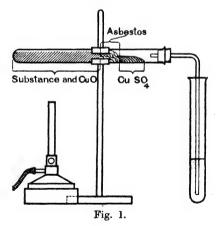



Fig. 1.

This is, of course, a "qualitative" combustion.

The presence of hydrogen can be determined as follows at the same time, if the substance be known to be free from water, combined or occluded, which is such a large requirement that it makes the test worthless, as has been said.

Put at the outlet end of the test-tube a quantity of dried and therefore anhydrous copper sulphate, keeping this part cool. Any water formed in the combustion unites with this, changing its colour to blue.

If a fixed residue remain in the ignition test, this shows the presence of metals, except mercury and arsenic—volatilised. In that case proceed as follows:—

Incinerate a larger quantity of the substance in a porcelain basin or crucible as completely as possible. Then extract all matter acted on by conc. HCl, filter, and proceed as usual for the metals.

This operation may result in the residue containing—

a. Metal reduced from compounds by the organic matter and so requiring solution in conc. acids, *e.g.* nitric.

β. Metallic compounds, mainly oxides, insoluble in conc. acids and therefore requiring alkali fusion previous to a complete analysis. The incineration should therefore be avoided wherever possible.

The only difficulties occurring in the precipitation by the ordinary schemes of the metals in Groups I. and II. in presence of organic matter arise from the possible co-precipitation of insoluble organic acids or quasi-acids, *e.g.* benzoic, salicylic acids, phenoloid bodies, etc., by the HCl and the H_2S.

The Group I. pp. may be extracted with an appropriate solvent—alcohol, ether—or submitted to steam distillation, the above co-precipitated bodies thus being removed.

The metals of Group III. form peculiar complexes with certain kinds of organic matter, oxalates (especially chromium), tartrates, citrates, other hydroxy-acids in general, and sugars.

Hence after the removal of the excess of H_2S from the filtrate from Group II., evaporate to dryness, adding oxidising agents such as conc. nitric or conc. HCl and $KClO_3$ crystals, thus destroying all kinds of organic matter. Then proceed with the analysis as usual.

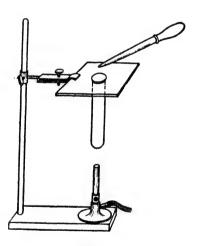
Metallocyanides (ferro-, ferri-, cobalti-, chromi-, etc.) are not completely decomposed so, but these can generally be identified by the particular reactions of the negative metallocyanogen complex.

Or: fuse with a mixture of ammonium nitrate and sulphate. This may leave oxides, etc., insoluble in acids, so should be avoided, if possible.

Nitrogen. Sulphur. Halogens.

On considering in detail the various forms in which nitrogen, sulphur, and the halogens occur in organic compounds, it will be seen that in general the presence of these can be determined by finding the presence of a certain functional group, *e.g.* amine, amide, sulphonate, halogen ester, etc., in the body: in this operation something is also learnt about the nature of the body. So that in general a previous determination of the elements present should be unnecessary: or if found necessary, this should be considered as a confession of failure to identify the functional groups present, by the scheme of analysis given.

Fig. 2.

In the above ignition test, the presence of nitrogen may be suggested, but not proved, by the production of a peculiar smell generally compared to that of burnt feathers (which contain nitrogenous matter). Also—Sulphur may be indicated by the production of sulphur dioxide, identified by its smell in the tests.

The presence of these can be determined by—

Sodium Fusion.

Support a hard glass ignition tube vertically by a clamp, or, better, by pushing it tightly through a hole in a piece of asbestos board (Fig. 2). Drop in a piece of sodium, clean and dry, the size of a pea. Heat the lower end of the tube to redness so as to produce a layer of the purple sodium vapour. Then add gradually about five drops of the substance if liquid—from, say, a fountain-pen filler—or dust in an equivalent quantity of solid directly on to the bottom of the tube. A slight but generally harmless explosion may result.[1] Let the tube cool and wash out, or, while still hot, dip vertically downwards into cold water—the tube in this latter case breaks up into fragments. Filter.

The nitrogen is now present as cyanide, sulphur as sulphide, and halogens as halogenide.

Divide into three portions.

For Nitrogen. Boil for a minute or so with a few drops of caustic soda and a drop or two of ferrous sulphate solution. Dissolve up the iron hydroxides with just enough dil. HCl, then add a slight excess of ferric chloride. Stand for a few minutes. Note any pp. (of Prussian blue), thus proving nitrogen. If the liquid appears green only, filter and examine residue on the paper.

For Sulphur. To about 1 c.c. of the filtrate add two or three drops of freshly prepared nitroprusside solution. An immediate and intense purple colour proves sulphur. Or add a few drops of alkaline lead acetate solution to the filtrate. A black pp. (PbS) shows sulphur.

Nitrogen and sulphur together might have given thiocyanate in the fusion, but not if sufficient sodium at a high enough temperature had been used.

Acidify 1 c.c. of the filtrate with dil. HCl, and add two or three drops of ferric chloride—a blood-red colour indicates thiocyanate: therefore sulphur and nitrogen together.

[1] Perhaps not always either slight or harmless. Consider what might happen in the case of nitro bodies, *e.g.* dinitrobenzene, picric acid!

For Halogens. Apply the usual tests if sulphur and nitrogen are proved absent.

But in any case the following method is better:—

Reduction Test for Halogens.

Dissolve a small quantity of the substance in absolute alcohol. Add pieces of sodium, waiting until each piece disappears before adding the next. Thus the halogen is replaced wholly or partly by hydrogen, the former combining with the sodium and possibly forming a pp. of Halogenide. Mix with a little water, boil off most of the alcohol, divide into four portions. Acidify each with dilute HNO_3.

Test (α) with dil. HNO_3 and $AgNO_3$—halogens generally. A brown pp. here (Ag_2S) proves again the presence of sulphur.

Test (β) with chlorine water and CS_2—bromine or iodine.

Test (γ) with bromine water—iodine.

Test (δ) with copper sulphate and ferrous sulphate—white pp. proves iodine.

CHAPTER II.

PHYSICAL PROPERTIES.

These for organic bodies are more purely personal to the definite substance than the chemical ones, and therefore are of more use for distinguishing and identifying particular members of a class, to which the substance has been found to belong by chemical class reactions, than for any other purpose.

The most obvious one is of course the state of aggregation, whether solid, liquid, or gas. The latter states occur naturally among the lower members of each class, as a rule, the higher ones being solids; but in some cases the first member is a solid, or more than one is, next members liquids, the m.p. falling to rise again. In some groups—*e.g.* higher fatty acids—the m.p. does not rise regularly, but in zig-zag fashion. The gaseous state is confined almost exclusively to the lower aliphatic hydrocarbons, only a few other aliphatic cpds. being gaseous and no aromatic cpd. at all.

The determination of the exact m.p. and b.p. of a substance therefore comes near or at the end of its examination. But a rough idea of the fusibility of a solid can be obtained from the ignition test; and of the volatility by evaporating a drop or two in a watch-glass in the air or letting it evaporate on the hand: very volatile substances have a distinct cooling effect.

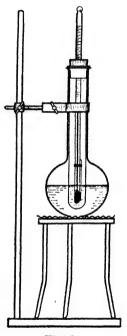
1. **Determination of Melting Point.**

A 200 c.c. round-bottom flask has a test-tube resting by its lip on the flask neck. Both are filled to the same height with a clear liquid. This may be conc. sulphuric up to 220°; and for higher temperatures, to about 350°, a mixture made by boiling for 5-10 minutes 70 parts conc. sulphuric with 30 parts K_2SO_4, or 55 of acid with 45 of $KHSO_4$; this is about as thick as glycerol: it does not fume badly nor affect rubber bands.

The substance is contained in a thin-walled capillary tube, made by drawing out a piece of wide-bore tubing, *e.g.* broken t.t., at the blowpipe. Pieces are then cut off of a convenient length, and closed at the end. The capillary is charged by pushing it mouth downwards into a little heap of the substance, turning it over and knocking the closed end against the table or rubbing the tube against the edge of a file. It is then fixed to the thermometer so that the substance is opposite the middle of the thermometer bulb, either by a rubber band cut from a piece of narrow tubing, or by a platinum wire, or simply by surface tension, wetting both with a drop of the bath liquid, when they will adhere. The thermometer and tube are then lowered into the test-tube, being held in position by a cork in the t.t. mouth, notched as shown to allow escape of air (Fig. 3).

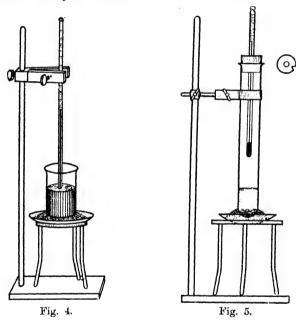
Fig. 3.

The flask is heated over gauze or a sand-bath at a rate depending on the nature of the substance—slow if it be stable, say 2° per minute for the last five degrees—at a rapid rate to near the m.p., then rather slower, if unstable. At last the substance becomes fluid and transparent, the thermometer being then read. Repeat with another sample. Take mean value.

Another method, best for substances unaltered in air and necessary for those that may explode (*e.g.* picric acid), is as follows:—

A little heap of the substance is put upon a microscope cover slip (or piece of thin mica) floating on a quantity of mercury in a little beaker heated on a sand-bath (Fig. 4). The bulb of a thermometer is just covered by the mercury and the temperature is read as usual. This method is limited of course by the temperature at which mercury begins to sublime in quantity, about 250°.

Either operation may be repeated with another—not the same—sample.

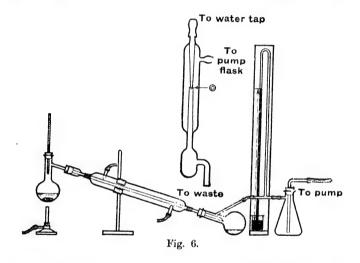
To ascertain whether two substances, samples of each of which melt near one another, are really the same, make a mixture of a little of each and take the m.p. of a sample of the mixture. If the substances are different, the m.p. will be depressed below that of either; if they are the same, it will be the mean.

Fig. 4. Fig. 5.

Find the m.p. of p-toluidine, naphthalene, acetanilide, sucrose powder, anthracene, anthraquinone, the last two only in capillary tube, the others by both methods. Compare the results.

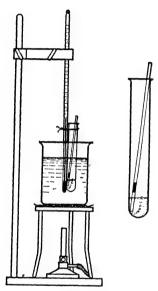
Find the m.p. of a sample of m-nitraniline. Mix about equal parts of this and acetanilide. Note m.p. Then mix two samples of acetanilide, one not perfectly pure. Find the m.p.

2. Determination of Boiling Point.

This can in general be determined approximately enough as follows :—A t.t. about 15 × 1·8 cm. is fitted with a cork carrying the thermometer and notched at the side. Liquid to the depth of 4 cm. (7 c.c.) is put in, so that it mainly condenses higher up the t.t. and runs back; with it are a few small pieces of porous pot. The tube is heated in a water-bath or on a sand-bath (Fig. 5). A round-bottom flask with long neck is better;

Fig. 6.

then all the mercury column of the thermometer is in the vapour, which condenses and runs back as before. Thus the correction for exposed stem is rendered unnecessary. For more accurate work a distilling flask fitted to a condenser and receiver is used, this being necessary if the liquid is to be fractionated, or if it decomposes when distilled under atmospheric pressure and so has to be boiled under reduced pressure (Fig. 6).

The receiver then is another distilling flask, the side tube of which is connected with a T-piece, one limb of which communicates with the pump flask and so with the pump. The manometer consists of an inverted ∩, with limbs of unequal length,

the longer, about 80 cm. to the bend, dipping into a dish of mercury, the shorter connected with the T. The difference between the height of the mercury in this tube and the barometric height at the time of experiment is of course the pressure under which the substance is boiling, at the temperature given by the thermometer. This is corrected for stem exposure by taking the reading of an auxiliary thermometer fixed to the exposed part of the stem of the other. Then, if n be the length of exposed stem in degrees, T° and t° readings of thermometers inside and outside, the true b.p. is

$$T + n\,(T - t) \times \cdot 000154.$$

Also, for pressures not normal from 72 cm. to 78 cm. the correction is $\pm \cdot 1^\circ$ for 2·7 mm. difference.

When only very small quantities of liquid are available, use one of the following methods:—

Fig. 7.

Siwoloboff's Method.—A thin-walled glass tube about $6 \times \cdot 7$ cm., fastened to a thermometer, beside the bulb, by wire, contains a few drops of the liquid and a capillary tube sealed near one end (Fig. 7). This is heated slowly in a suitable bath. Bubbles come from the lower end of the capillary, and when these form a continuous stream the thermometer is read. Repeat with a fresh capillary, etc.

Chapman Jones's Method.—A thin-walled tube (Fig. 8, *a*) shaped like a little siphon barometer but with the open limb longer than the closed one, has a few drops of liquid in the closed limb, the tube then being heated in a suitable liquid boiling higher than the specimen; the open end dips into a small beaker of mercury *b*, to which the tube is fixed by a wire sling, the whole being hung over the bath by a rod *c*. As the specimen boils, all air is removed, the tube, on cooling, remaining filled with mercury

with the exception of a bubble of condensed liquid at the bend. When cold remove the tube from the Hg, closing the end with the finger. Invert it so that the liquid passes into the closed end. Push out Hg from the open limb with a glass rod, so that the level is lower than in the closed end. Then put into the bath again and heat, with stirring, until the Hg level in both limbs is the same; then read the thermometer. Continue heating for a short time: let cool and read thermometer with Hg at same level again.

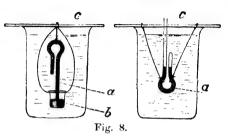



Fig. 8.

Find the b.p. of: (*a*) ethyl alcohol by method (1) using water; (*b*) aniline (on sand-bath); (*c*) ethyl tartrate in vacuum (known); (*d*) naphthalene, method (3); (*e*) toluene, method (4) using glycerol as bath in latter cases.

3. Determination of Specific Gravity.

It is seldom necessary to determine the specific gravity in identifying a substance: such information as that the liquid is lighter or heavier than water being determined among the first tests on mixing with water. High specific gravities can generally be noticed on handling the specimen.

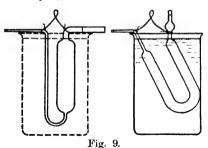



Fig. 9.

When that of a liquid must be found, the most convenient apparatus is some form of Sprengel tube as drawn. The tube is weighed empty, *i.e.* full of air, then full of water at an observed temperature, then full of the liquid at a standard temperature. The tube

is filled by suction so that, *e.g.* in the form to the left of Fig. 9, the liquid extends from the drawn-out end to the mark on the other limb, the quantity being adjusted, (i) if it is too small, by applying a drop on the end of a rod to the drawn-out end while holding the tube in an inclined position, or, (ii) if it is too large, by applying a piece of filter-paper to the drawn-out end, in each case until the meniscus of the liquid comes to the mark: other forms are filled in a similar manner. Corrections are made for the weight of air in the tube (at least) and the weight of water is corrected to maximum density, *i.e.* 4°, the final result being expressed thus, $D^{20°}_{4} = x$, if 20° were the temperature of the experiment.

4. Determination of Optical Activity.

This determination is required in distinguishing between dextro and levo optical isomerides, and it is sometimes useful in distinguishing between cpds. not optical isomerides, but nearly allied chemically, like glucose and fructose.

5. Determination of Electrical Conductivity.

This determination is seldom necessary for the identification of organic cpds., though it gives useful information concerning the basicity of polybasic acids—by the changes on dilution in the conductivity of their salts. Many organic substances are non-electrolytes in solution.

ALIPHATIC GROUP.

CHAPTER III.

THE HYDROCARBONS.

SATURATED HYDROCARBONS. THE PARAFFINS, C_nH_{2n+2}.

The earlier members are colourless gases, increasingly easier to liquefy; higher are liquids, colourless, with peculiar smell, volatile unchanged; the highest are solids, less and less soft, *e.g.* vaseline and paraffin wax, distilling unchanged only in partial or complete vacuum.

Gases only slightly soluble in water, the rest not at all. All soluble in alcohol, more or less easily in other organic solvents.

Use *Ligroin* for tests and note above characters.

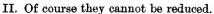
I. *a.* All very combustible, flame increasingly luminous and smoky. The highest leave carbon residue.

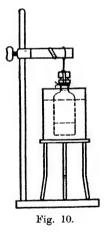
Burn some ligroin on a thin glass rod.

They resist wet way oxidation.

c. Warm a little ligroin with alkaline $KMnO_4$ in a stoppered bottle in water bath (Fig. 10). Any brown turbidity is due to oxidation of impurities.

Fig. 10.

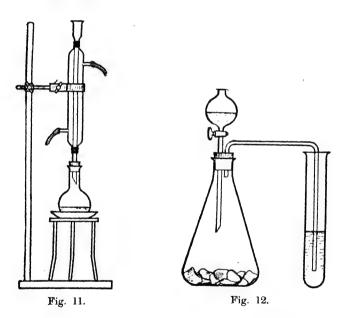
II. Of course they cannot be reduced.

III. Nor can they form addition products.

Warm a little with conc. H_2SO_4: no result: immiscible.

V. With halogens, substitution cpds. are formed.

Mix a few c.c. with bromine and a few iron nails in a small flask (Fig. 11). Boil under reflux for a time. Note the HBr evolved, therefore substitution has occurred.

XIII. Nitration (and sulphonation III. above) do not occur, nor hydrolysis.

Warm with conc. HNO_3, and with conc. KOH. No action in either case.

Fig. 11. Fig. 12.

UNSATURATED HYDROCARBONS. *a.* ETHYLENES, C_nH_{2n}.

In appearance and in solubility these are similar to the above.

Use *amylene*, C_5H_{10}, and note the above characters.

I. *a.* All very combustible; flame generally more luminous and smoky than for corresponding paraffin.

Try it as usual.

They are all easily oxidised in the wet way.

c. Heat as above in stoppered bottle with $KMnO_4$. Result: much turbidity.

II. Reduction means addition of hydrogen, as with nascent hydrogen (H_2 and Pt).

III. Addition reaction showing unsaturation.

a. Mix with bromine water, warming: it is decolorised.

c. Mix with conc. H_2SO_4, warming for a time, pour into water, boil and distil. Test for amyl alcohol (*q.v.*).

d. The above *c.* is an indirect way of adding water.

e. Addition of hydrogen, as above, II.

V. *a.* Halogens do not in general replace hydrogen, they are added on—III.

IX. Hydrolysis is not, of course, possible.

Warm with KOH Aq., no result; immiscible.

UNSATURATED HYDROCARBONS. *β.* ACETYLENES, C_nH_{2n-2}.

In appearance these are similar to the above, but are more soluble in water.

Use *acetylene* from CaC_2 and water.

I. *a.* All very combustible, flame smoky and luminous. Mixtures of acetylene and air are generally dangerously explosive.

c. Wet way oxidation: very easy.

† Pass the gas into warm alkaline $KMnO_4$ (Fig. 12): much turbidity.

II. Reduction, as for ethylenes above.

III. Addition as above, but to twice the extent.

†*a.* Bromine water: pass the gas into the warm reagent.

†*c.* Sulphuric conc.: pass the gas into the warm reagent. Pour into water. Boil, etc., as above, but test distillate for aldehyde (Schiff's Reagent).

IV. Cuprous chloride in ammonia gives yellow, brown or red pps. only with C_2H_2 and unsymmetrically substituted acetylenes, *i.e.* with those containing the grouping ·C ⋮ CH.

† Pass the gas into reagent in t.t., chocolate red pp. formed.

Boil the pp. with excess of KCNAq., acetylene is regenerated.

Tollens' reagent gives, similarly, white pps. of similar composition.

V. *a.* Halogens are added on, of course, as above.

c. At high temperatures sodium replaces the H of the ·C ⋮ CH group; in C_2H_2 in two stages.

IX. As above, for ethylenes.

XV. On heating under pressure they readily polymerise into benzene and its derivatives.

CHAPTER IV.

ALCOHOLS, HYDROXY BODIES.

MONO-HYDROXY ALCOHOLS.

Colourless liquids, mostly with characteristic smell, boiling unchanged at atmospheric pressure, except higher members. Lower members soluble in water, in solutions of alkalis and of their chlorides, also in $CaCl_2$Aq., insoluble in K_2CO_3Aq., soluble in organic solvents, unless diluted; higher members less soluble in water, etc.

Ethyl alcohol, C_2H_5OH, as type of Saturated or Paraffin Alcohols. Test its solubility as above.

I. *a.* Combustible, flame more luminous and smoky the higher the alcohol, highest members burn with smoky flame.

Oxidation products are characteristic for structure of alcohol as follows :—

Primary, RCH_2OH,	Secondary, RR'CHOH,	Tertiary, RR'R"COH,
Aldehyde, RHCO.	Ketone, RR'CO.	Two or more acids.

b. Dichromate. See Preparation of Acetaldehyde.

Warm the alcohol with $K_2Cr_2O_7$ powder and dil. H_2SO_4 in t.t. fitted with bent delivery tube. Distil over into a little water in another t.t., standing in cold water. Test the distillate with Schiff's Reagent. (Fig. 13.)

c. Alkaline Permanganate is completely reduced.

Test with above apparatus. Note turbidity and any aldehyde.

d. Fehling's Solution is not reduced.

Try with above apparatus.

e. Nitric acid conc. reacts with dangerous violence. The product from ethyl alcohol is oxalic acid.

II. *a*. Zinc dust, hot, gives corresponding hydrocarbon, *e.g.* ethyl alcohol gives ethane. Alcohols are not directly reduced otherwise.

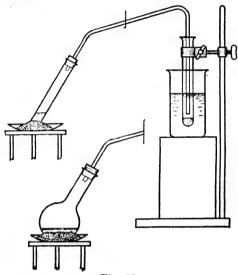



Fig. 13.

V. *b*. The halogens cause substitution, and, at the same time, oxidation. The products are various halogenated aldehydes, ketones, etc., hydrolysed by alkalis, so that ethyl alcohol, etc., give *e.g.* chloroform, iodoform.

Warm in t.t. with I in KI, adding KOH carefully until decolorised. A yellow pp. of characteristic smell is the iodoform.

c. Sodium replaces H of OH group forming Alkylates (*q.v.*).

Put 10 gm. absolute alcohol into a porcelain basin, add small pieces of sodium as long as each piece disappears rapidly. Hydrogen is evolved. When action becomes slow, evaporate rapidly to dryness. Reserve product.

VI. Phosphorus halogenide or P and halogen give haloid ester.
See Preparation of Ethyl Iodide.

VII. 1. Etherification.

a. Alkylsulphuric acid and alcohol *b.* Alkylate and alkyl haloid ester *c.* Alkyl iodide and silver oxide	all give ether	simple or mixed	according to the alkyl groups used.

See Preparation of di-Ethyl Ether.

3. Esterification.

a. Alcohol and acid *b.* Alkylsulphuric acid and dry Na salt *c.* Alkyl iodide and silver salt	all give esters	according to the particular	alkyl and acid radicals used in the reaction.

a. See Preparation of Ethyl Acetate.

b. Mix some absolute ethyl alcohol with about half its volume of conc. sulphuric, add a little dry sodium acetate and warm. Note smell of the ester.

4. Esterification by Acylation.

a. Add to some absolute alcohol in a t.t. a little acetic anhydride. Note smell of ester and of acetic acid.

VIII. Alcohols are not ionised in aqueous solution.
Test reaction to litmus : neutral if pure.

X. *a.* Elimination of water by conc. H_2SO_4.
See Preparation of Ethylene.

Methyl Alcohol, CH_3OH.

Note appearance and smell ; solubility as above.

I. *a.* Test combustibility as usual.
b. Test wet way oxidation as above.

II. *a.* Hot zinc dust gives methane.

V. *b.* No iodoform is formed unless it contains acetone, a common impurity.
c. Sodium acts as usual.

VI. It gives the normal reaction with phosphorus halogenides.

VII. 1. Etherification product is a gas, CH_3OCH_3.

3. *a*. Esterification : acid and alcohol.

Warm in t.t. with sodium salicylate and a little conc. H_2SO_4. Note smell of methyl salicylate.

4. *a*. Acylation with acetic anhydride.

Test as above. The methyl acetate smells similarly to ethyl acetate.

VIII. As above.

Propyl Alcohol, $CH_3CH_2CH_2OH$.

This is similar to ethyl alcohol in appearance and in smell when pure, but commercial samples smell of amyl alcohol. It has, of course, a higher b.p. than ethyl alcohol.

Note these points and the following :—

I. *a*. Flame more luminous.

V. *b*. Does not give iodoform easily.

VII. *b*. Its esters have a rather different smell.

X. *a*. Commercial samples often give a red colour with conc. H_2SO_4. See amyl alcohol.

***Butyl Alcohol,** primary, *i.e.* $CH_3CH_2CH_2CH_2OH$.

Similar to above, solubility in salt solution diminishes.

Amyl Alcohol, $C_5H_{11}OH$.

Commercial samples from fusel oil are mixtures of isomers, mainly primaries. A liquid of characteristic smell, more oily, less soluble in water, insoluble in NaCl or $CaCl_2$ solutions, higher b.p.

Note these points and the following :—

I. *a*. Combustible, flame luminous and smoky.

b. Oxidation as usual into aldehyde.

Apply test and identify product, as aldehyde, by Schiff's reagent.

V. *b*. No iodoform if pure.

VII. 1. Etherification as usual, but with more difficulty.

3. Esterification.

Make amyl acetate as for ethyl acetate. Note characteristic smell.

X. *a*. Conc. H_2SO_4 gives a red colour and a peculiar smell. (Only if commercial ?)

Confirm this.

***Secondary alcohol, Isopropyl** $(CH_3)_2CHOH$.

Liquid, b.p. lower than for propyl; smell, solubility as for propyl.

Reactions similar to above, but—

I. Oxidation (moderated) gives a ketone—acetone, CH_3COCH_3.

V. *b*. It gives iodoform easily.

***Allyl Alcohol,** $CH_2:CH.CH_2OH$ **as type of Unsaturated Alcohol.**

Liquid b.p. near that of propyl, pungent smell like mustard, sol. in water, etc.

Reactions as for primary alcohols.

I. *b*. Oxidation gives acrolein.

c. Alkaline permanganate gives glycerol.

III. Being unsaturated it gives addition reactions.

Add Br. Aq. to a sample. It is decolorised.

ALKYLATES OF MONO-ALCOHOLS, *e.g.* RONa.

These are solids; very deliquescent. They should be colourless, but commercial, *i.e.* old, specimens are yellow (see below).

Use *sodium ethylate* (ethoxide) already prepared above.

I. *a.* Partly combustible: flame colour that given by the metal.

IX. *a.* Soluble in and decomposed (hydrolysed) by water and dil. acids.

Mix with a little water, add a piece of porous pot, and distil off the alcohol (bent tube and t.t.); identify it. Residue contains soda, NaOH, strongly alkaline.

Other reactions as for alcohol, since so very easily decomposed by reagents used in these cases.

Try to get iodoform (not from CH_3ONa): also ethyl acetate: by usual methods given above.

With alkyl iodides, simple or mixed ethers are obtained.
Oxidation: slow, by air gives aldehyde resin (*q.v.*)—hence the yellow colour.

Ethers of Mono-Alcohols, ROR′.

These are colourless liquids, much more volatile than corresponding alcohol, smell "ethereal." Lower members soluble in water to some extent, insoluble in salt solutions and in alkalis.

The only important member is *di-ethyl ether*: use it: note above points.

I. *a.* Dangerously inflammable, being so volatile: flame luminous.

Confirm this.
Oxidation generally as alcohol.

II. Reduction also as alcohol.

V. Halogens, *e.g.* chlorine, can replace all the H atoms.

b. It gives no iodoform.

Try this.

c. Sodium has no action since it contains no (OH) group.

Try with pure dry ether: if any H be produced, water or alcohol is present, probably both.

VI. PCl_5, with great difficulty, gives halogen ester, C_2H_5Cl.

IX. It is hydrolysed by conc. acids, in which it dissolves, *e.g.* cold conc. H_2SO_4.

d. Especially by conc. hydriodic, see Zeisel's method.

b. It is not hydrolysed by alkalis.

Poly-hydroxy-Alcohols.

***Di-hydroxy alcohols,** *e.g.* **Glycol,** $CH_2OH.CH_2OH$.

This is a colourless liquid, thick, and with a sweet taste. B.p. high. Soluble in water. Volatile with steam. It gives normal reactions, but may of course give them in two stages.

Tri-hydroxy alcohols, *e.g.* **Glycerol,** $CH_2OH.CHOH.CH_2OH$.

A thick, colourless, odourless liquid with sweet taste. High b.p., with slight decomposition generally. Soluble in water and salt solutions, insoluble in ether. Volatile with steam.

Confirm these observations.

I. *a.* Not very combustible, flame non-luminous; too much oxygen in it.

Try it as usual.

b. Oxidised by dichromate, products not characteristic; also by permanganate.

d. Fehling's Solution is not reduced even after boiling with acids. See Sugars.

Try this. Compare sugar syrup, also thick and sweet.

g. Medium conc. nitric acid gives glyceric and oxalic acids.

II. *h.* Heated with oxalic or formic acids, it is reduced to allyl alcohol at high temperatures. With oxalic at lower temperatures, formic itself is produced.

See Preparations of these substances.

k. Heated with white phosphorus and iodine, either isopropyl iodide, allyl iodide or propylene is produced, according to the conditions.

See Preparations of these substances.

V. Replacement of H by halogen or by Na, not characteristic, and, in latter case, slow.

VII. 3. A mixture of conc. nitric and sulphuric acids gives "nitroglycerine" a nitric acid ester.

4. Forms esters by acylation : products not characteristic.

Many animal and vegetable fats and oils are its esters with high aliphatic acids.

VIII. Reaction neutral to indicators; therefore no ionisation. But it reacts with inorganic acids forming ester-acids, which if formed from weak acids are so much stronger than the original that they can be titrated, *e.g.* in presence of glycerol, boric acid can be titrated with phenolphthalein.

X. *a.* Elimination of water.

Mix some glycerol with conc. H_2SO_4, it dissolves. On heating, better with $KHSO_4$, it gives acrid-smelling "Acrolein" an unsaturated aldehyde. Distil some over into water as usual; apply Schiff's reagent.

Mix with dry oxalic acid and heat; at first formic acid is given off. As the temperature is raised allyl alcohol is given off: note its smell. Distil over a little and apply the tests (see *ante*).

***Hexa-hydroxy-alcohols,** *e.g.* **Mannitol,** $C_6H_8(OH)_6$.

This is a white sweet solid. It is closely related to the sugars, but it does not reduce Fehling's solution even after boiling with acids.

Prove that this is so.

CHAPTER V.

ESTERS OF INORGANIC ACIDS.

A. HALOGEN ESTERS, MONO-HALOGEN DERIVATIVES OF THE HYDROCARBONS.

These are colourless liquids with a more or less sweet smell, volatile unchanged at lower b.ps. than corresponding alcohol, heavier than and insoluble in water, insoluble in aq. solutions, soluble in organic solvents.

Methyl chloride and bromide, and ethyl chloride are gases at ordinary temperature.

Ethyl Bromide as Type of Saturated Halogen Esters.

Note above properties.

I. *a*. They are not very combustible, and the flame often shows evidence for halogen; green or blue edge.

Test as usual.

c. They are not in general oxidised without hydrolysis, then as alcohol.

Warm in stoppered bottle with alkaline $KMnO_4$. Note any turbidity.

II. *e*. Reduction by Zn/Cu couple gives the corresponding hydrocarbon.

Fit one limb of a U tube with a dropping funnel, the stem passing down the limb, and the other limb with a delivery tube dipping under water. Fill this limb with the Zn/Cu couple. Drop in a mixture of EtBr and EtOH (1:1) by the funnel. Collect the ethane over water. Pass part of it into hot alkaline $KMnO_4$. The U tube should stand in cold water. (Fig. 14.)

f. Reduction by sodium. Halogen is removed, the alkyl residues uniting.

Sodium and alcohol give the corresponding hydrocarbon and sodium halogenide.

V. *a*. Further action of the halogens gives di-haloid cpds. symmetrical or unsymmetrical, according to conditions.

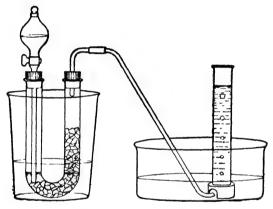



Fig. 14.

VII. 1. *b*. With alkylate, RONa, they give ethers, simple or mixed.

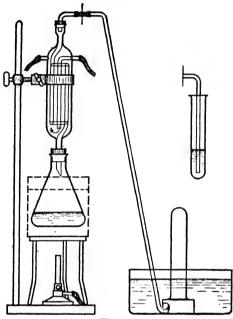
2. *a*. With alcoholic NH_3, they give primary, secondary, tertiary, and quaternary amines.

3. *c*. With Ag salts, they give Ag halide and alkyl ester.

VIII. The iodo cpds. only, are ionised in alcoholic soln., the reaction in water or with other halides being incomplete.

Dissolve in alcohol, add alcoholic $AgNO_3$. Note results.

IX. *b.* Hydrolysis by alkalis gives alkali halide and corresponding alcohol.

Fig. 15.

Put into a small flask fitted to a reflux condenser 10 c.c. EtBr and 40 c.c. KOH solution. Boil, with pieces of porous pot, over a water-bath until the layer of EtBr has disappeared. Turn down the condenser and distil off from a sand-bath. Identify halogen ion in residue. Separate unchanged EtBr from distillate by adding excess of NaCl. Identify alcohol by I. *b.*

X. *b.* Alcoholic KOH gives ethylenic hydrocarbon by eliminating HX.

Put 10 c.c. EtBr with 50 c.c. alcoholic KOH into a small flask fitted to reflux condenser from the top of which passes a delivery tube dipping under water. Boil over a water-bath. Identify the ethylene by passing it into Br.Aq. and into warm conc. sulphuric acid. (Fig. 15.)

c. Hot zinc dust removes halogen, the alkyl residues uniting in part; and it also in part replaces hydrogen so as to give the corresponding hydrocarbon.

Isopropyl Iodide, $(CH_3)_2CHI$, **as Type of Secondary Haloid Ester.**

A colourless liquid with peculiar smell. Solubility as usual. Reactions quite normal. Hydrolysis gives the alcohol, *q.v.*

Allyl Iodide, $CH_2 : CH . CH_2I$, **as Type of Unsaturated Haloid Ester.**

A colourless liquid, smelling like mustard. Rather more soluble than usual.

Hydrolysis gives the alcohol (*q.v.*).

Being unsaturated, it forms addition products.

Mix a little with Br.Aq. This is decolorised.

Note.—All iodine organic cpds. turn brown on keeping, owing to the liberation of iodine by the action of light and air.

B. Poly-Halogen Esters. Di-haloid Esters.

Alkylene, $\alpha\beta$ or 1. 2.

These are colourless heavy liquids, with sweet smell, volatile unchanged at much higher b.ps. than mono cpds. They are insoluble in water, in aq. salt solutions and dil. acids, soluble in organic solvents.

Use *ethylene di-bromide,* CH_2BrCH_2Br. Note above points and the following:—

I. *a.* It is nearly incombustible.
Test as usual.

c. Oxidation as mono-derivative.
Try, as in that case, with alkaline permanganate.

II. *f.* Reduction by sodium and alcohol.
Mix a little with alcohol (4 vols.), add pieces of Na, as long as they dissolve rapidly. Identify halogen as usual.

VII. 1. *b.* With alkylates it gives glycol ethers, of course.
3. *c.* With silver salts it gives glycol esters normally.
} In two stages according to quantities used.

VIII. Like the other haloid esters it is not appreciably ionised. Test as for ethyl bromide.

IX. *b*. On hydrolysis it gives glycol, $C_2H_4(OH)_2$.

X. *b*. Elimination of HX. With alcoholic KOH in excess it loses 2HBr, giving acetylene.

Test as for ethyl bromide, using 5 c.c. of the dibromide and 25 c.c. alcoholic KOH. Identify the acetylene by cuprous chloride in ammonia.

* **Alkylidene,** *αα*, *ββ*, etc.

These are colourless liquids, with a much less pleasant smell than the above and a much lower boiling point. They are much more easily hydrolysed than the above (even slowly by water) into aldehydes (*αα*) and ketones (*ββ*, etc.), whence they are derived by the action of PCl_5, etc. Their reactions therefore are normal.

C. Tri-Haloid Esters, Chloroform Group.

Chloroform, $CHCl_3$.

This is a heavy colourless liquid with a very sweet smell, volatile without decomposition, miscible with alcohol and ether, very slightly soluble in water, insoluble in alkalis and in salt solutions.

Note above points and the following :—

I. *a*. Nearly incombustible.
Test as usual.

b. Acid dichromate, hot, gives carbonyl chloride, $COCl_2$, a colourless gas with a most unpleasant smell.

d. It reduces Fehling's soln., because of its conversion into formic acid.

Confirm these statements.

II. *f*. Reduction : as for other haloid esters.

Repeat experiment with sodium and alcohol, as under Ethyl Bromide.

VII. 1. *b.* With alkylates it gives ethers, called "Orthoformic Esters."

VIII. In aqueous or even in alcoholic soln. it is not ionised appreciably.

Apply the ordinary test for halogen ions.

IX. *b.* Hydrolysis gives formate and chloride.

Boil in small flask under reflux condenser as for ethyl bromide. Remove condenser and test residue for chloride as usual and for formate, *q.v.*

XIII. *h.* See Isocyanide Reaction under Aniline.

**Bromoform* is a thick liquid, turning brown on standing, of much higher b.p. than chloroform. Reactions quite similar.

Iodoform is a yellow crystalline powder or scales, with characteristic smell and definite m.p., insoluble in aqueous liquids, soluble in alcohol and in ether.

It gives reactions quite similar to those for chloroform.

Prove the presence of iodine in it by sodium and alcohol as usual.

D. Tetra-Haloid Esters.

Carbon Tetrachloride, $C Cl_4$.

This is the only important one. It is a mobile colourless liquid, boiling unchanged at a low b.p. Commercial samples often contain CS_2 and smell like that. Otherwise the smell is sweet. Solubility as for chloroform.

Note these points and the following :—

I. *a.* It is quite incombustible.

Test as usual.

c. It resists wet way oxidation.

Heat in stoppered bottle with alkaline $KMnO_4$: any reduction due to impurities.

II. *f.* Reduction as for the other haloid cpds.

Repeat experiment with sodium and alcohol. Complete reduction takes a long time. Any brown pp. of Ag_2S is due to sulphur impurity.

VII. 1. *b*. Etherification by alkylate gives "Ortho-carbonic Esters."

VIII. It is not ionised in soln.

Try the usual test.

IX. *b*. Hydrolysis is rather difficult, but in time KOH (better alcoholic) gives chloride and carbonate.

Boil a few c.c. with excess of alcoholic KOH under reflux condenser. Try to identify the products.

E. Esters of other Inorganic Acids.

a. Those in which the H atoms of the acid are all replaced by alkyl (etc.) groups are colourless liquids, more or less soluble in water, insoluble in salt solutions, soluble in organic solvents, volatile sometimes without decomposition.

They are all hydrolysed by boiling with aq. alkalis into alcohol (one or more molecules) and a salt of the organic acid, and by this operation they are identified.

Ethyl Nitrite, C_2H_5ONO.

The real substance is a liquid, b.p. 16°. "Sweet Spirit of Nitre," the commercial representative used in medicine, is a mixture containing some aldehyde, alcohol, and water. The real substance may explode under certain conditions.

I. Oxidation results, obviously not characteristic.

II. Reduction gives alcohol, and hydroxylamine or ammonia.

Nitro-cpds. give *amines*.

IX. It may give ordinary reactions for nitrites without formal hydrolysis, but it will give them in any case after boiling with aq. KOH.

Add $FeSO_4$.Aq. and dil. H_2SO_4; the usual brown coloration is obtained.

Add KI,Aq.; iodine is set free, identified as usual.

"*Nitroglycerine*" is really a nitrate ester, hydrolysing normally.

Methyl Sulphate, $(CH_3)_2SO_4$.

A colourless liquid, without much smell, but very poisonous, even the vapour. It dissolves to some extent in water. It is used in the operation called Methylation, *i.e.* replacement of H of OH or NH_2 or NH groups by CH_3 groups. Its reactions are quite normal.

The others are of little importance.

β. Those in which the H atoms of the acid are only partially replaced by alkyls are ester-acids, *i.e.* behave as acids and esters.

F. Inorganic Ester-Acids.

Alkylsulphuric Acid, RSO_4H, **and Salts.**

The acids themselves, not important, are generally uncrystallisable liquids, very deliquescent, very soluble in water and in alcohol. The salts are crystalline solids, often deliquescent, all soluble in water and many of them in alcohol and so quite different from the corresponding sulphates.

Use *potassium ethylsulphate* and note above properties.

I. *a*. Of course it is not very easily combustible.

Test this by heating on a piece of porcelain or of Pt foil. Test the wetted residue with litmus paper—acid, *i.e.* $KHSO_4$.

b. Wet way oxidation succeeds only by precedent hydrolysis.

Apply usual test with acid dichromate: note result.

c. Try also alkaline permanganate in a stoppered bottle.

II. *a*. Reduction with hot zinc dust gives sulphide, so that the residue if wetted with acid smells of H_2S.

Confirm this.

VII. 1. *a*. The acid heated with alcohols gives ethers, the ordinary method of preparing these.

3. *b*. The acid heated with haloid or organic salts gives esters, a common method of preparing these, *e.g.* ethyl bromide.

VIII. The negative ion of the acid and salts is $(C_2H_5SO_4)'$, but this ion forms no insoluble salts. When pure, the alkali salts have a neutral reaction.

Test with $BaCl_2$ and a little dil. HCl. There is generally only a slight cloudiness, due either to K_2SO_4 as impurity or to incipient hydrolysis by the dil. HCl.

IX. *b*. It is hydrolysed into sulphate and alcohol by boiling with alkalis.

Carry out a formal hydrolysis with KOH as for ethyl bromide, using 15 gm. salt and 50 c.c ordinary KOH solution. Apply the tests to the distilled alcohol and to the sulphate in the residue.

The other ester-acids are quite similar to the above in their behaviour.

CHAPTER VI.

ALDEHYDES AND KETONES.

A. ALDEHYDES, RHCO.

The lower members are colourless liquids, with pungent smell, volatile unchanged at b.ps. much lower than the corresponding alcohol. They are soluble in water and in organic solvents.

Formalin is a 40 per cent. aqueous soln. of the gaseous formaldehyde, H_2CO.

Samples of *acetaldehyde* are often aqueous-alcoholic solutions of CH_3HCO.

Use both of these for the following reactions, where applicable.

a. The gas H_2CO is of course combustible: so is the ordinary acetaldehyde.

Try acetaldehyde. In neither case is the flame very luminous.

b. Acid dichromate gives corresponding acids.

Warm some acetaldehyde with the oxidising mixture in a stoppered bottle. Distil the mixture so as to isolate the acid and identify this.

d. They reduce Fehling's Soln.

Warm specimens of the aldehydes with it: red pp. of Cu_2O.

e. They reduce Tollens' Reagent.

Mix in a very clean t.t., warm in water-bath: silver mirror.

h. They are oxidised by atmospheric oxygen; samples therefore generally contain corresponding acid.

Test with litmus.

II. *f*. Nascent hydrogen (sodium amalgam and water) gives primary alcohol.

V. Halogenation is generally accompanied by oxidation.

VI. Phosphorus pentachloride gives alkylidene dichlorides, $RHCCl_2$.

XIV. 1. *a.* Their aqueous solns. seem to contain alkylidene glycol $RHC(OH)_2$: by addition of water.

b. They add on NH_3 generally. Formaldehyde condenses with it, forming hexamethylene tetramine $(CH_2)_6N_4$ (*q.v.*).

See Preparation of Acetaldehyde and of Hexamethylene Tetramine.

c. They add on HCN, forming nitriles of hydroxy acids R.HCOH.CN. These on hydrolysis give the corresponding acids, R.HCOH.COOH.

d. They add on sodium hydrogen sulphite, forming hydroxy-sulphonates, $R.HCOH.SO_3Na$, as solid crystallisable cpds., from which the aldehydes are easily obtained by adding dil. acids or alkaline carbonates.

e. They combine with one another, forming hydroxy-aldehydes, $R.HCOH.(CH_2)_n(HCO)$. This is the Aldol reaction, and may be followed by elimination of water, resulting in the formation of an unsaturated aldehyde, $RHC:CH(CH_2)_nHCO$. This happens on standing for a time with conc. HCl (aldol), then heating.

f. They combine with acyl anhydrides, forming alkylidene di-esters.

2. The following condensation reactions are possibly preceded by addition reactions similar to the above.

a. They condense with hydroxylamine when the HCl salt is mixed with the aldehyde and dry sodium acetate, forming aldoximes. These are colourless liquids, distilling unchanged, and behaving as quasi-acids, dissolving in alkalis. With acetic anhydride they give alkyl cyanides by dehydration.

b. They condense with phenyl hydrazine and with hydrazine itself under similar conditions, forming phenylhydrazones, RHCNNHPh, and hydrazones, $RHCNNH_2$, and aldazines, RHCN.NCHR.

c. They condense with mercaptans, forming mercaptals, $RHC(SR')_2$.

d. They condense with one another, forming unsaturated aldehydes. See 1. *e.*

e. They condense with alcohols on heating, forming ethers called Acetals. These are colourless liquids boiling unchanged. They are hydrolysed by boiling with conc. acids, so regenerating the aldehyde. The commonest member, acetaldehyde diethyl ether, $CH_3HC(OC_2H_5)_2$, is itself called *Acetal.* It is a liquid, with a characteristic smell, obtained as a bye-product in the manufacture of acetaldehyde.

f. With conc. alkalis they give yellow, resinous substances with peculiar smell—"aldehyde resin." Formaldehyde behaves like an aromatic aldehyde here, giving methyl alcohol and formate. Compare Benzaldehyde.

Try with acetaldehyde.

g. They condense with Schiff's Reagent in the cold on standing, giving red or violet-red cpds.

Confirm this: formalin gives a more violet colour than acetaldehyde.

XV. Under certain circumstances they polymerise into complex bodies, some of which are ring cpds., *e.g.* paraldehyde, and do not give the aldehyde reaction until depolymerised.

Allow a few c.c. formalin soln. to evaporate in the air: there remains a white solid, paraformaldehyde.

Add a drop or two of conc. H_2SO_4 to 1 c.c. of acetaldehyde. The mixture becomes hot, and on adding water paraldehyde separates as an oily liquid.

Commercial specimens of paraldehyde are thick liquids, smelling of aldehyde, which break down on boiling with water, at least in part, into aldehyde.

Commercial paraformaldehyde is a white powder smelling of H_2CO.

Distil samples of both with water: test distillate with Schiff's Reagent.

Trichloracetaldehyde or Chloral, CCl_3HCO, **and its Hydrate,** $CCl_3HC(OH)_2$.

The substance is an oily liquid of pungent smell, with definite b.p.; its hydrate is a crystalline solid of characteristic smell and taste, with definite m.p., decomposing about the b.p. of chloral itself.

The reactions are mainly those of the unsubstituted body, with those belonging to a halogen ester.

I. *a.* It is not very combustible.

Test as usual.

g. Conc. nitric acid, hot, gives trichloracetic acid.

See Preparation of this.

II. Nascent hydrogen removes the halogen, as well as alters the HCO group.

V. It cannot be further halogenated.

VIII. The Cl atoms are not present as ions in aqueous soln.

Dissolve some of the hydrate in water, test for halogen ion as usual.

IX. *b.* Alkaline hydrolysis gives chloroform, even in the cold.

Shake up a little chloral hydrate with caustic soda. Note the formation of oily drops smelling of chloroform.

XIII. *h.* For the above reason, it gives the isocyanide reaction.

XIV. 1. It shows all the ordinary aldehyde addition reactions and a number of others as well.

a. Chloral itself combines with water into the perfectly definite stable hydrate. Its cpd. with alcohol is the end product of the chlorination of alcohol, and from that chloral itself is obtained.

2. It shows also most of the aldehyde condensation reactions. It gives, of course, no "aldehyde resin."

B. Ketones, RCOR′.

The lower ketones are colourless liquids, each with its own peculiar smell, volatile unchanged at low b.ps. They are soluble in organic solvents, and with gradually diminishing extent in water; insoluble in salt solution and in alkalis.

Dissolve some acetone in water and add common salt in excess; the acetone separates out as an upper layer, *i.e.* it has been "salted out."

They show the following reactions: to be applied to—

Acetone, Di-methyl Ketone, CH_3COCH_3.

I. *a.* They burn with rather luminous flame, especially the higher ones.

Try as usual with acetone.

b. They are oxidised in the wet way, less easily than aldehydes.

Acid dichromate gives acetic acid, CO_2, and water—from acetone.

Boil 5 c.c. of acetone with the mixture in a small flask under a reflux condenser until the acetone smell has gone. Turn down the condenser, distil the volatile part; test it for acetic acid.

d. Ketones do not reduce Fehling's Soln., nor

e. Tollens' Reagent.

Try with Fehling's Soln., boiling.

II. *f*. Reduction of acetone with sodium amalgam and water gives isopropyl alcohol, and pinacone,

$$(CH_3)_2COH.COH(CH_3)_2,$$

with insufficient hydrogen.

Measure out 30 c.c. of acetone, mix with 120 c.c. of water, put into a stout, well-stoppered bottle. Slowly add 850 gm. of sodium amalgam of good quality in small pieces, shaking vigorously all the time, waiting until the effect of each piece has ceased. When hydrogen begins to be evolved, pour off from the mercury and distil the aqueous liquid, collecting all below 95°. Salt out with K_2CO_3, standing over-night. Distil off and dehydrate over CaO: thus isopropyl alcohol is obtained. The pinacone may crystallise out from the residue, in plates, smelling like peppermint.

V. *a*. Chlorine passed into boiling acetone gives symmetrical dichloracetone, $CH_2Cl.CO.CH_2Cl$.

b. Bleaching powder when boiled with acetone gives chloroform.

See Preparation of the latter.

Apply the iodoform test to acetone; it succeeds better than it does with ethyl alcohol.

VI. Phosphorus pentachloride with ketones gives cpds. of type $RR'CCl_2$.

X. *a*. Methyl ketones when heated with conc. sulphuric eliminate water, forming symmetrical tri-alkyl-benzenes; thus acetone (3 mols.) gives up (3 mols. of) water, forming mesitylene, symmetrical trimethylbenzene, $C_6H_3(CH_3)_3$.

XIV. 1. Ketone addition reactions.

a. The addition of water is not so definite as with aldehydes.

c. The addition of HCN gives nitriles of tertiary HO-acids. RR′COH.CN. These on hydrolysis give the corresponding acid, RR′COH.COOH.

d. With sodium bisulphite:—

Make a saturated solution of SO_3NaH, add acetone slowly, cooling under the tap until the cpd. comes out; let stand; filter with pump; press well until dry.

Mix some of the cpd. with conc. Na_2CO_3 soln.; distil from sand-bath. Collect the acetone, salt out with $CaCl_2$; dry and distil. Note b.p.

2. Ketone condensation reactions.

a. With hydroxylamine.

See Preparation of Acetoxime.

Acetic anhydride converts these ketoximes into acetic esters, RR′CNOAc.

b. With phenylhydrazine forming phenylhydrazones. With hydrazine forming hydrazones, and ketazines, RR′CN.NCRR′.

c. With mercaptans forming mercaptols, $RR'C(SR)_2$. These are oxidised to sulphones. That from acetone and ethyl mercaptan is *sulphonal*, the soporific.

d. Ketones by the action of conc. KOH condense, forming more complex ketones; thus acetone forms mesityl oxide, $C_6H_{10}O$, and phorone, $C_9H_{14}O$.

h. Acetone condenses with NH_3, forming diacetonamine, $(CH_3)_2CNH_2CH_2COCH_3$, and triacetonamine, $C_9H_{16}(NH)O$.

j. Colour reaction for acetone.

Mix a few drops of fresh sodium nitroprusside solution with acetone and a little water; add ammonia and shake: a violet or violet-red colour appears gradually.

Hexamethylene Tetramine, $(CH_2)_6N_4$.

This is used in medicine. It acts as a weak base, forming salts, of which the urate is rather soluble (for a urate). Boiled with dil. H_2SO_4, formaldehyde distils over, leaving $(NH_4)_2SO_4$, whence NH_3 is separated by alkalis. It may be identified in this way.

The Aldehyde Ammonias.

These are colourless crystalline cpds. (acetaldehyde-NH_3 smells of mice), which very easily give up aldehyde when distilled with dil. acids, or with alkalis give NH_3 and the "resin." This identifies them. They turn yellow on keeping.

CHAPTER VII.

CARBOHYDRATES.

These contain their H and O present in the proportion necessary to form water, hence the name given to the group.

The only important members are—

Glucose or dextrose, fructose or levulose, galactose, all $C_6H_{12}O_6$.

Sucrose or cane sugar, lactose or milk sugar, maltose, all $C_{12}H_{22}O_{11}$.

Cellulose, starch, dextrin, simplest formula $C_6H_{10}O_5$.

The latter two certainly of much more complex formula.

As to structure, part of the O and of the H is present as OH groups, so that all are polyhydroxy alcohols.

Glucose, lactose, galactose, and maltose are also mono-aldehydes.

Fructose is also a mono-ketone.

Sucrose is also an ether.

These statements are proved by their reactions.

A. Sugars.

Glucose, $C_5H_6(OH)_5HCO$.

From aq. solution this crystallises in colourless crystals + H_2O, from alcohol in white crusts, anhydrous. In ether and in other organic solvents it is insoluble. It has a definite m.p. It is less sweet than cane sugar.

I. *a.* Its flame is slightly luminous and a residue of shining charcoal is left.

Test by heating on a piece of platinum foil or of thin porcelain.

Wet way oxidations.

d. Fehling's Soln. is readily reduced on warming, as also is copper acetate, Barfoed's Reagent.

Confirm these statements.

e. With Tollens' Reagent it gives a silver mirror.

Mix in a well cleaned t.t., warm in a beaker of water.

g. On heating with conc. nitric acid, oxalic acid is formed.

k. With bromine and Na_2CO_3, a monobasic acid, gluconic $C_6H_{12}O_7$, is obtained. Hence glucose is a mono-aldehyde.

II. *f*. With sodium amalgam and water it adds on H_2, forming sorbitol, $C_6H_{14}O_6$, a hexa-hydroxy-alcohol, another proof that it is a mono-aldehyde.

j. On heating with fuming HI in a sealed tube, iso-hexyl iodide is obtained. This connects glucose with the hydrocarbons.

VII. 1. Ethers occur in nature, the glucosides, and some of these have been made artificially, *e.g.* methyl glucoside.

4. Acylation. With acid chlorides or anhydrides, *e.g.* acetyl or benzoyl, pentacetyl or pentabenzoyl esters are formed, and with an anhydride, 5 molecules of acid are eliminated per molecule of glucose, which proves that it is a pentahydroxy-alcohol, *i.e.* it contains 5 (OH) groups.

VIII. Its aq. solution shows no sign of ionisation.

IX. It cannot be hydrolysed.

X. *a*. Elimination of water. Conc. sulphuric dissolves it at first to a clear solution containing a glucose-sulphuric acid, but the mixture soon becomes brown, then black by charring. This may happen at once with commercial samples.

Try this, first cold, then warming gently.

XII. *a*. It dissolves easily in lime water, forming a definite cpd. used in its separation from other substances.

XIV. 1. Aldehyde addition reactions:—

a. It crystallises with one molecule of water from aq. solution.

b. It does not combine with ammonia.

c. It does add on HCN, forming the nitrile of a hydroxy-acid, from which by hydrolysis that acid is obtained, and from this the next higher aldehyde sugar can be obtained.

d. It does not combine with sodium hydrogen sulphite easily.

2. Aldehyde condensation reactions:—

a. Glucoseoxime is formed quite normally.

b. With phenylhydrazine it gives a dihydrazone called an osazone, as for other sugars. These are yellow well-crystallised substances, of definite m.p., used in characterising the different sugars.

Mix 2 gm. of phenylhydrazine with an equal volume of glacial acetic, and dilute to 20 c.c. Mix this with a solution of 1 gm. of glucose in 10 c.c. of water. Heat the mixture on a water-bath. In a few minutes a crystalline mass of the osazone is formed. Filter it off, wash with water and dry it.

e. See VII. 1.

f. With conc. alkalis a yellow to brown liquid is produced, similar to "aldehyde resin."

Warm a little glucose with NaOH soln.

XVII. Fermentation by yeast.

Fit a 2 litre flask with bent delivery tube dipping into some lime water in a bottle. Put into the flask 10 gm. of glucose in 200 c.c. of water and about 30 gm. of brewers' yeast. Keep in a warm place (about 25°). Note the frothing, due to CO_2, which soon reaches the lime water. Filter into a smaller flask. Distil off the aqueous alcohol. Let it stand over K_2CO_3. Separate the alcohol and identify it.

Levulose or Fructose, $C_5H_7(OH)_5CO$.

Ordinary specimens are wet-looking, brown masses, more sweet and more soluble in water than glucose, less soluble in alcohol, generally insoluble in other organic solvents.

I. *a*. As glucose.

Wet way oxidising agents (mild) break it up into trihydroxybutyric and glycollic acids. This proves that fructose is a ketone.

d, *e*. With Fehling's solution and Tollens' reagent it behaves like glucose.

Repeat these tests with fructose as with glucose.

g. Conc. nitric converts it into oxalic acid, as for sugars in general.

II. *f*. With sodium amalgam it gives mannitol and sorbitol.

j. Like glucose, it passes into isohexyl iodide with hot fuming HI; obviously it is a derivative of the same hydrocarbon.

VII. 4. On acylation as for glucose, it gives penta-acyl derivatives. Fructose therefore is a pentahydroxy alcohol, as well as glucose.

VIII, IX. As for glucose.

X. *a*. Elimination of water.

Ordinary specimens are charred fairly readily by conc. sulphuric.

Try this test in the usual way.

XII. *a*. Like glucose, it dissolves readily in solns. of Ca and Sr hydroxides forming cpds. used in the separation from other sugars, in particular from glucose, the lime cpd. of which is more soluble in water.

XIV. Ketone reactions.

1. *b, c, d*. As glucose.

2. *a, b*. As glucose; the osazones are found to be identical.

XVII. Like glucose, it is fermented by yeast, only more slowly, and if glucose be present the fructose is attacked only after that has been nearly used up.

Sucrose, *i.e.* **Cane Sugar,** $C_{12}H_{22}O_{11}$.

This is a crystalline solid, non-deliquescent, very sol. in water, slightly sol. in alcohol, insol. in ether. It has a definite m.p. but begins to decompose slightly above that.

Cautiously melt a quantity in a t.t. Let it cool. Note that on solidification it forms a glassy mass, "barley sugar," which devitrifies (crystallises) on standing. Heat another part until it becomes brown and is converted into "caramel."

I. *a*. It burns with a luminous flame, leaving a residue of "sugar charcoal."

Try this as usual.

d, *e*. It is not oxidised either by Fehling's Soln. or by Tollens' Reagent.

Confirm these statements.

g. Conc. nitric acid gives at first saccharic acid and finally oxalic.

Heat 125 gm. of conc. nitric acid to 100° on the water-bath in a large flask. Remove from the bath and add 25 gm. of sugar. Torrents of brown fumes are evolved. When these cease to come off, the liquid is evaporated on the water-bath to one-quarter of its bulk. On cooling, large colourless crystals of oxalic crystallise out. Drain these at the pump and re-crystallise from a small quantity of water. Finish as usual.

VII. 4. Acylation. With acetic anhydride it gives an octacetyl derivative; it is therefore an octo-hydroxy alcohol.

VIII. Its solns. show no sign of ionisation.

IX. *c*. Hydrolysis by acids. It gives a mixture of glucose and fructose in equal proportions, "invert sugar."

Boil a quantity of sugar with a little dil. HCl. Neutralise, then prove that the mixture reduces Fehling's Soln.

See also Preparation of Glucose.

It has not yet been found possible to make glucose and fructose condense directly to form sucrose. This hydrolysis by acids suggests that sucrose is an ether.

X. *a.* Elimination of water. Conc. sulphuric acid chars it at once, especially if warm. Cp. *pure* glucose and lactose.

Make a strong sugar syrup with a little warm water. Pour into it a small quantity of conc. H_2SO_4. The mixture blackens, swells up very much with evolution of steam, and leaves a porous mass of charcoal.

XIV. It is neither an aldehyde nor a ketone, as it gives none of the reactions characteristic of these groups.

XVII. The "invertase" present in yeast first hydrolyses it to "invert sugar," then this mixture ferments as usual.

It can also give lactic acid by the appropriate ferment.

Lactose or Milk Sugar, $C_{12}H_{22}O_{11}$ or $C_{11}H_{13}O_2(OH)_8HCO$.

This crystallises from water as a monohydrate. The substance itself has a definite m.p., but decomposes if heated above that. It is nearly insol. in alcohol, quite so in ether. It is only faintly sweet.

I. *a.* It behaves like the other sugars on combustion.

d. Fehling's Solution }
e. Tollens' Reagent } are reduced as by glucose, but to a less extent relatively.

Barfoed's Reagent, *i.e.* copper acetate, is not reduced.

Try these experiments as usual, confirming the above statements.

Mild oxidising agents, *e.g.* Na_2CO_3 and Br_2, give an acid containing the same number of C atoms and one O atom more; hence lactose is a monoaldehyde.

VII. 4. Esterification by acylation, *e.g.* with acetic anhydride, it forms an octoacetyl derivative; hence it is an octo-hydroxy-alcohol.

VIII. In solution it is not ionised.

IX. *c*. Hydrolysis by boiling with dil. acids produces equal quantities of glucose and of another C_6 sugar, galactose.

Hence lactose is an ether of these sugars, but the union is such as to leave one aldehyde group still present. Compare sucrose, in which the aldehyde group of glucose and the ketone group of fructose have both been lost.

X. *a*. Most specimens are readily blackened by conc. H_2SO_4, especially if hot.

Try this.

XIV. Aldehyde reactions.

1. It gives addition reactions similar to those of glucose (*q.v.*).

2. It gives condensation reactions similar to those of glucose (*q.v.*).

f. When warmed with conc. alkali solutions, it gives a brown colouration.

Try this.

XVII. It does not easily ferment with yeast, but certain bacteria convert it into lactic acid, as in sour milk, and other bacteria give butyric acid.

B. Carbohydrates not Sugars.

Starch, $(C_6H_{10}O_5)_n$.

This is a white powder, made up of microscopic grains (cells) of organised structures of various kinds, each characteristic of the plant from which it came. It is not quite certain whether the "n" is the same for all varieties.

Like cellulose, it retains water tenaciously. It is insoluble in water until, on long boiling, the cell-walls are broken, when the inner material forms an opalescent pseudo-solution, from which alcohol precipitates the so-called "soluble starch."

Boil a quantity of potato starch with water for some time. Let stand and then pour off from the sediment. Add some alcohol to part of the solution. Use the rest of this solution and some raw potato starch for the tests.

I. *a*. It burns with a pale flame, leaving a charcoal residue.

d, *e*. It is not oxidised by these reagents.

Confirm these statements.

g. Hot conc. nitric gives oxalic acid finally.

VII. 3. Esterification by acids, *e.g.* conc. sulphuric dissolves it at first and chars it only after long heating.

Try the reaction.

VIII. The physical properties of the pseudo-solution suggest a very high molecular weight, *i.e.* "n" is high in all forms of the substance.

IX. *c*. On hydrolysis by boiling with dil. acids for some time, maltose and dextrin (*q.v.*) are the first recognisable products, then only glucose.

Boil some starch paste in a small flask with dil. sulphuric for some time, testing small samples removed occasionally for dextrine, and for glucose by applying Fehling's Soln., after neutralisation.

XIV. Starch shows neither aldehyde nor ketone reactions.

XVII. Starch ferments only after hydrolysis, as by the "diastase" of malt or the "ptyalin" of saliva, which convert it into sugars.

Add a few c.c. of malt extract to 20 c.c. of starch paste, warm to 60° for a time, testing samples, removed at intervals, with Fehling's Soln. At last reduction occurs.

The most striking reaction after its behaviour with water is that with iodine in KI soln., the nature of which is unknown.

Add the I soln. to some cold starch paste; it turns a deep blue. Warm the mixture; the colour disappears, but it reappears on cooling. The colour disappears on adding $Na_2S_2O_3$ Aq. by removal of the iodine.

*** Dextrin** $(C_6H_{10}O_5)_n$, "n" not very large.

Ordinary specimens are yellowish-white amorphous powders, soluble in water to gummy opalescent solutions, tasteless; the dextrin is re-ppd. by alcohol. Most samples contain starch and reducing sugars, so may give erratic reactions.

I. *a.* It burns quite in a similar manner to starch.

d, e. These reagents are not reduced by pure specimens.

IX. *c.* Hydrolysis by dil. acids gives glucose.

X. *a.* Conc. sulphuric chars most specimens rapidly.
Iodine in KI dil. gives in general only a red colour.
Work over the above tests.

XVII. It ferments only after hydrolysis, as by diastase.

Cellulose, $C_6H_{10}O_5$ or $(C_6H_{10}O_5)_n$.

A white fibrous substance of structure characteristic of its particular plant source. It retains water with some firmness and also encrusting materials from the original plant ash, fat, etc., separable mechanically or chemically. It is insoluble in all ordinary solvents.
Use clean white cotton-wool or Swedish filter-paper.

I. *a.* It burns with nearly non-luminous flame, leaving some charcoal and ash.

d, e. It is not oxidised by these reagents.
Confirm these statements.

VII. 3. Esterification by acids. Conc. sulphuric dissolves it to sol. sulphates.

Try this. See also IX.

Conc. nitric in presence of conc. sulphuric forms various nitrates.

4. Acylation by acetic anhydride gives an ester, triacetyl if cellulose be written $C_6H_{10}O_5$.

IX. *c.* On long boiling with dil. acids sugars are formed, glucose generally, especially from the sulphates (above).

Boil a sample of cellulose as above until the mixture after neutralisation reduces Fehling's Soln.

Parchment paper is obtained by soaking ordinary unsized paper in medium conc. H_2SO_4 for a sufficiently long time.

b. Alkaline hydrolysis changes the substance only slightly, the result appearing to be merely hydration. This is known as "Mercerisation."

XIV. It gives none of the ordinary aldehyde or ketone reactions; therefore its molecule contains no such structures as these.

It is dissolved by an HCl solution of $ZnCl_2$; also by Schweizer's Reagent, being ppd. by acids from the latter solution unchanged except as to form, *i.e.* as a gelatinous pp., like $Al(OH)_3$.

Most varieties are coloured deep blue or violet by Schultz's Soln., *i.e.* by iodine in $ZnCl_2$, not by I in KI.

Try these two tests.

Cellulose nitrates are formed without apparent alteration in structure. The lower ones (mono and di-nitrate for $C_6H_{10}O_5$) dissolve in alcohol-ether, the solution being *collodion*, and drying up to a transparent film. The higher one (trinitrate similarly) is *guncotton*, insoluble in alcohol-ether, sol. in acetone or "nitro-glycerol." Such solutions are used in smokeless powder, "*cordite.*" This one is explosive on percussion, but all are highly inflammable.

On boiling with dil. KOH, all regenerate cellulose; therefore they are true esters, like "nitro-glycerine," and not nitro-bodies.

CHAPTER VIII.

ACIDS.

Mono-Carboxy-Acids. Type RCOOH.

REACTIONS COMMON TO THE GROUP.

The lower members are sol. in water and in salt solns., but this solubility decreases with rise in molecular weight. They are sol. in organic solvents, but their solutions in water are not miscible with these.

I. *a*. Their combustibility increases to a certain extent in ascending the series, but the highest members are ignited with difficulty and burn with a very smoky flame.

II. *a*. Reduction to hydrocarbon may happen on heating their salts with excess of zinc dust.

b. Reduction to aldehyde happens on heating their Ca salts with Ca formate, both well dried, under reduced pressure if necessary.

Make an intimate mixture of calcium acetate and sodium formate. Put into a hard glass tube lying horizontally and fitted with bent delivery tube touching the surface of a little water in a t.t. kept cold by a bath. Heat strongly. Test distillate for aldehyde by Schiff's reagent (Fig. 1). Or use apparatus like Fig. 16, in which the distillate is cooled by a condenser.

When the Ca salts are heated alone similarly they give ketone. Formate alone gives formaldehyde, H_2CO.

V. *a*. Halogens replace H attached to C, the halogen going to the C next the COOH group, in the first instance.

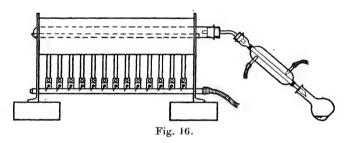
See Preparation of Chloracetic Acids.

b. Sodium, etc., of course replace the carboxyl H, but no H may be evolved owing to interference by other groups present.

Dissolve a little stearic acid in dry ether in a t.t. fitted with delivery tube and kept cool by a water bath. Drop in pieces of sodium. Collect the H_2 over water and identify it.

VI. Phosphorus halogenides replace OH groups by halogens generally. The simple acids give acyl chloride, but with more complex acids further decomposition may and often does occur.

See Preparation of Acetyl Chloride.

Fig. 16.

VII. 3. Esterification. See under each acid.

VIII. Carboxy-acids are not in general strong, *i.e.* well ionised, especially mono, and the ionisation recedes as the series is ascended. Their sol. salts are generally ionised so that they give the reactions for the acid ion.

IX. Only certain substituted acids can be hydrolysed.

The soluble salts are hydrolysed to some extent, so that solutions of these are often alkaline to indicators like methyl orange or even litmus. This is very largely the case with the salts of the higher acids, *e.g.* the soaps, hence their use as detergents.

Try the reactions to methyl orange and to litmus of solutions of sodium formate, acetate, stearate, *i.e.* hard soap.

X. *a*. Hydroxy acids lose water, forming either unsaturated acids or else anhydrides of various kinds. See those acids.

The ammonium salts all lose water on heating, producing various acid amides.

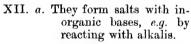
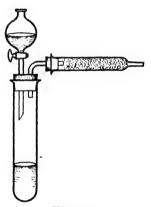
See Preparation of Acetamide.

b. Halogen substituted acids give up HX to alcoholic KOH, leaving unsaturated acids.

d. All acids and their salts give up CO_2 to hot soda lime, the simple acids producing hydrocarbons—those next lower in the series.

Mix thoroughly by grinding together 20 gm. of fused sodium acetate and 50 gm. of soda lime. Put into a hard glass flask lying horizontally and fitted with a delivery tube. Heat strongly. Collect the gas over water. Note its flame in air and test it as for a saturated hydrocarbon.

Fig. 17.

XII. *a*. They form salts with inorganic bases, *e.g.* by reacting with alkalis.

Fit a large t.t. with cork carrying a small dropping funnel and an open soda lime tube. Put into the tube 25 c.c. N/10 NaOH, free from CO_2 and just coloured with phenolphthalein. Dissolve some stearic acid in alcohol, drop this in gradually, with shaking. The acid reacts with the alkali: the colour is discharged (Fig. 17).

Other acid reactions are considered under each acid.

Acetic Acid, CH_3COOH.

Glacial acetic is a crystalline solid, m.p. 16·05° when quite anhydrous, but the presence of even a little water lowers the f.p. considerably, so that most samples are liquid. It has a characteristic pungent smell. It is perfectly miscible with water, aq. solns., alcohol, and with organic solvents if undiluted. Its salts are solids and none of the normal ones are really insol. in water; many of them dissolve also in alcohol.

Use glacial acetic, sodium acetate, fused and $+3H_2O$. Confirm the above.

I. *a.* The conc. acid burns with a pale flame, leaving no carbon, but the salts are hardly combustible, giving off acetone, or acetic acid itself if from heavy metals.

Confirm this, using copper acetate for the latter part.

Neither the acid nor its salts can be oxidised in the wet way.

VII. 3. *a.* Esterification. Acid and alcohol with conc. H_2SO_4 as dehydrator.

See Preparation of Ethyl Acetate.

b. Salt of acid and alkylsulphate.

Mix well in a mortar fused sodium acetate and potassium ethylsulphate. Heat in a hard glass tube. Smell the ethyl acetate vapour evolved.

XII. *a.* Dil. acetic decomposes carbonates.

Try the effect of 30 per cent. acid on marble, calcite, chalk. Try the glacial acid also.

b. The acid is set free from its salts by distilling with conc. mineral acids.

Make acetic acid from fused sodium acetate as nitric acid is made from nitre. Rectify by redistillation over more of same acetate.

c. The basic ferric acetate is insoluble in water.

Add $FeCl_3$ to a soln. of a salt, but not to the acid; a red colour is produced. Boil, acetic is given off and a red pp. is formed.

The salts when heated with arsenious oxide give cacodyl oxide, recognised by its disgusting odour.

Heat small quantities together in an ignition tube closed by the finger. Then reject the tube and smell the finger!

Formic Acid, HCOOH.

A pungent smelling liquid of definite f.p. when quite anhydrous, but ordinary samples contain water, greatly depressing the f.p. Solubility of acid and salts quite like that of acetic acid.

Use formic acid soln. and sodium formate. Note above and the following..

I. *a*. Unless dil. the acid burns with a pale flame. The salts are hardly combustible, giving off H_2 and leaving no charcoal.

Try the above.

b. Oxidation with acid dichromate. *c*. Oxidation with alkaline permanganate.

Heat acid in stoppered bottle with each of these. Note results.

d, *e*. Fehling's Soln. and Tollens' Reagent.

Warm the acid with these in t.ts. Both are reduced, a silver mirror being obtained from the latter.

Other oxidations are characteristic.

Warm the acid with mercuric oxide. A grey pp. of Hg, and CO_2 evolved. With mercuric chloride the salts give a white pp. of Hg_2Cl_2. Try this.

These reactions are exceptional and depend on the HCO group present.

VII. 3. Formic esters are obtained as usual, but with HCl gas as dehydrator.

X. *a*. Conc. H_2SO_4 causes evolution of CO by elimination of water, etc.

Heat the acid and its salts with conc. H_2SO_4. Identify the CO by flame.

d. With hot soda lime, a carbonate remains, hydrogen being evolved.

Heat sodium formate with soda lime. Identify the hydrogen.

XII. *a.* The acid forms salts, *e.g.* by decomposing carbonates.

Dilute a sample well, boil and dust in lead carbonate as long as it dissolves easily. Let cool; the salt crystallises in needles.

Find the strength of a sample of the acid by titration against N/10 caustic soda, using litmus, after appropriate dilution.

b. Inorganic acids remove it from its salts.

Prepare the pure acid from dry lead formate by dry H_2S. See Preparation.

c. Formation of insol. salt, basic ferric formate.

Try as under Acetic Acid.

**Propionic Acid* is in general more or less similar to acetic, but it is insol. in $CaCl_2$ soln.

* The *higher acids* acquire a greasy smell, *e.g.* butyric, valeric, noticeable to some extent also in their salts, which sometimes show also a greasy lustre, and are hydrolysed by water, to a greater and greater extent.

* *Unsaturated acids* show reactions both for the COOH group and for the unsaturated linkage. Thus *Acrylic Acid* adds on two atoms of halogen forming 1, 2 di-halopropionic acid, or one molecule of halogen hydride HX or of H.OH, the X or OH going to the 2- or β-C, *i.e.* as far as possible from the COOH group, forming thus β- halo- or HO- propionic acid. See below.

Substituted Acids.

These are $\alpha, \beta, \gamma, \ldots$ or $1, 2, 3, \ldots$ substituted acids according to the position of the substituents, relative to the COOH group.

When they are produced by direct substitution of an acid, the halogen (for example) always replaces H attached to the α-C atom. Thus propionic gives α-monobrom-propionic, then $\alpha\beta$-dibrom-propionic, etc.

Halosubstituted acids. Chloracetic Acids as examples.

The mono- and tri- chloracetic acids are deliquescent solids, dichloracetic a liquid, all boiling progressively much higher than acetic. Solubility in general similar to that of acetic. Their salts are similar to acetates.

They have of course two functions, being carboxy acids and halogen esters. Typical reactions for each group can be obtained.

I. *a*. They are much less combustible than acetic: influence of the halogens.

II. Reduction is reverse substitution.

Prove that chloracetic acid contains chlorine (Na and alcohol).

VII. 3. *c*. Salts of monochloracetic with potassium cyanide give salts of cyanacetic from which malonic by hydrolysis.

See Preparation of Malonic Acid and its esters.

VIII. These acids are progressively much stronger than acetic, *i.e.* much more fully ionised. Trichloracetic is as strong as the strong mineral acids. The halogen is not present as ions in soln.

Test monochloracetic in the ordinary way with $AgNO_3$.

No result.

IX. Hydrolysis of monochloracetic as an ester gives glycollic, of dichloracetic glyoxylic, and chloride, but—

Trichloracetic and its salts when shaken with alkalis give chloroform and carbonate; compare chloral.

Try this. Identify $CHCl_3$ by smell, etc.

X. *b*. Monohalogen acids with alcoholic KOH lose HX, giving olefine unsaturated acids. Dihalogen acids with alcoholic KOH lose 2HX, giving acetylene unsaturated acids, unless these changes are impossible from the structure.

XIII. *h*. For the above reason (IX), CCl_3COOH and its salts give the isocyanide reaction.

Try this, with aniline and excess of KOH.

Mono-Hydroxy Acids. Lactic Acid as type.

Lactic acid is α-hydroxypropionic, $CH_3CHOHCOOH$. The ordinary acid is a thick syrup of sour smell, uncrystallisable, very sol. in water and in alcohol, sol. in ether, decomposed on distillation except in a vacuum. It is optically inactive, being a mixture of the dextro and levo forms. Its salts are solids, often crystalline, all sol. more or less.

I. *a*. The acid is combustible, its salts partially so, both charring somewhat. Both acid and salts are easily oxidised in wet way, products normal.

II. *j*. The acid is reduced by hot conc. HI to propionic acid.

V. *c*. Sodium replaces the H's of the OH and COOH groups, forming a so-called basic lactate, $CH_3.CHONa.COONa$. Water hydrolyses this into $CH_3.CHOH.COONa$ and NaOH. Compare ethylates and the change of NaO-COONa into HOCOONa and NaOH (below).

IX. *c*. Hydrolysed by medium conc. sulphuric; the acid and salts give acetaldehyde and formic acid (or CO by dehydration).

Distil a small quantity of acid with 50 per cent. H_2SO_4 (bent tube and t.t.), collecting the products in water. Identify acetaldehyde and the CO as usual.

X. Acids of this group can eliminate water in various ways depending on the position of the OH group. See Chapter XXX. *a*. Lactic acid itself gives *Lactide*, a ring ether-ester-anhydride, of definite m.p. and b.p.

XII. The acid reacts with hydroxides and decomposes carbonates. It is obtained from its heavy metal salts by precipitating metals by H_2S, filtering and evaporating. From alkaline earth salts by precipitating metal by dil. H_2SO_4, then as above. From alkali salts by adding dil. H_2SO_4, extracting with ether, etc.

Carbonic Acid. This is hydroxyformic acid and it is the first member of this series. From its symmetrical structure it is a dibasic acid, but its sol. normal salts are alkaline, being hydrolysed so that the solns. contain $M(HCO_3)$ and $M(OH)$, *i.e.* their ions. Also the free acid is unstable, its two OH groups being attached to the same C atom as in ethylidene glycol $CH_3CH(OH)_2$. The elimination of water usual in such cases here produces CO_2, the reaction by which carbonates are recognised.

DI-CARBOXY ACIDS.

There are two classes here :—

*1. Those having the two COOH groups attached to the same C atom, as Malonic and its homologues.

Their most important properties are :—

On heating they lose CO_2, forming the corresponding mono-carboxy-acid, *e.g.* malonic $CH_2(COOH)_2$ gives acetic.

The H, if any, attached to this same C atom is replaceable by (for example) sodium, *e.g.* malonic esters give $CHNa(COOR)_2$ and $CNa_2(COOR)_2$.

By the action of many different kinds of halogen cpds. on these Na derivatives other cpds. are prepared, Na halide being eliminated.

These reactions are of extreme importance in syntheses.

In their other reactions the acids of this class react normally.

2. Those having the two COOH groups attached to different C atoms.

Of this class a typical example is:—

Succinic Acid, $\begin{array}{l} CH_2COOH \\ \vert \\ CH_2COOH. \end{array}$

A colourless crystalline solid of definite m.p. At slightly higher temperatures part sublimes, the rest forming anhydride. The acid is sol. in water and in alcohol, less sol. in ether. The acid and its sol. salts have a disagreeable characteristic taste.

Use succinic acid and sodium succinate.

I. *a.* The acid burns with a blue flame, leaving little or no charcoal. Its salts may char, however, and alkali ones leave a carbonate.

Confirm these statements.

Acid and salts resist wet way oxidation well.

V. *a.* Hydrogen attached to C is replaced by halogens in all cases fairly easily, sometimes, as in the case of succinic, in definite steps. This gives mono- and di-brom-acids, the latter of symmetrical constitution.

c. Replacement by sodium should happen in two stages, forming mono- and di-sodium cpds.: they are not prepared in this way, of course.

VI. Replacement of OH by the action of phosphorus halides cannot generally be carried out in two stages, and sometimes, as in the case of succinyl chloride, the expected symmetrical cpd. reacts as if it were unsymmetrical.

VII. 3. *a, c.* Esterification may happen in two stages, these two methods being used. The products of the first stage behave as ester acids, giving a set of salts quite different from those of the acid itself. See "Esters."

VIII. The dibasic acids are in general more fully ionised than the monobasic ones, but the two H ions have not always equal value, *i.e.* they are not set free at the same dilution nor in any case to the same extent. Acid or hydrogen salts give three ions, *i.e.* they have an acid reaction—compare the monalkyl esters where the (−) ion contains alkyl.

Succinic is a medium strong acid. Its hydrogen or acid salts behave as monobasic acids—see Oxalic Acid.

X. *a.* On heating these dicarboxy acids, with or without a dehydrating agent, water is eliminated, an anhydride being formed; unless there are four or more CH_2 groups between the two COOH groups, in which case the acid melts without losing water, and

may volatilise without doing so either, *e.g.* adipic $HO_2C(CH_2)_4CO_2H$. $POCl_3$ is used as the dehydrator generally.

With hot conc. sulphuric acid, succinic acid and its salts do not char except on very prolonged heating.

Confirm this.

XII. *a.* Succinic decomposes carbonates.

b. It is obtained from its salts as oxalic acid, *q.v.*

c. It forms various insol. salts.

Add $BaCl_2$ and alcohol to sodium succinate soln.: white pp.

Add $FeCl_3$ to sodium succinate soln.: flesh-coloured basic pp.

XIII. When the acid is heated with resorcinol and a little conc. H_2SO_4, cpds. like the phthaleins (*q.v.*) are formed.

Warm gently, pour the melt into water, make alkaline: red colour.

Oxalic Acid, COOH.COOH.

This is a colourless crystalline substance, crystallising from water with $2H_2O$, this being the cpd. $C(OH)_3 . C(OH)_3$. This dissolves in warm conc. H_2SO_4, the anhydrous acid crystallising out. It loses the water also on heating. It is sol. in water, less so in alcohol, much less so in ether. By careful heating to 150° the acid may be sublimed, but generally a part decomposes into formic acid and CO_2. The salts are solids, only those of the alkalis being sol. in general; only a few crystallise anhydrous like KHC_2O_4. All are sol. in acids.

Confirm these statements, using $H_2C_2O_4, 2H_2O$, etc.

I. *a.* The acid is not combustible. Salts decompose without charring. Those of the alkalis evolve CO, which burns, of course, leaving carbonate. $Ag_2C_2O_4$ passes with a mild explosion into finely divided silver and CO_2.

Confirm this.

a. Oxalates are oxidised quantitatively by $KMnO_4$ (or MnO_2) and dil. H_2SO_4, as in volumetric analysis.

b. Oxidation with dichromate is incomplete owing to the formation of stable chromoxalates, *e.g.* $K_3Cr(C_2O_4)_3$.

III. *d*. The acid and many salts combine with water of crystallisation, and there are super-acid salts like potassium quadroxalate, $KH_3(C_2O_4)_2$.

V. *a*. Replacement of H by halogen is impossible, of course.

VI. PCl_5 causes decomposition by dehydration, forming $POCl_3$, HCl, CO, and CO_2, mainly.

VII. 3. *a*. Esterification as usual, with HCl gas as dehydrator. See remarks on Succinic Acid.

VIII. Oxalic is a strong acid, nearly as strong as the strong mineral acids. Its solns. can therefore be titrated, using litmus, but not methyl orange.

Make N/10 KHC_2O_4 and titrate caustic soda soln. with it, using phenolphthalein.

IX. Solns. of its normal salts are neutral to most indicators, *i.e.* are not appreciably hydrolysed. KHC_2O_4, etc., are acid, of course.

X. *a*. The acid and salts heated with conc. sulphuric evolve CO and CO_2.

Try this, using the acid, ferric oxalate, and potassium chromoxalate.

XII. *a*. In aq. soln. the acid and KHC_2O_4 decompose carbonates rapidly.

Weigh out 15 gm. of acid, dissolve in hot water, add potassium carbonate until neutral to litmus. Divide into two equal parts. Evaporate one down until it crystallises; thus $K_2C_2O_4.H_2O$. Filter at pump, and dry as usual. To the other part add 7·5 gm. more oxalic. Evaporate, to obtain crystals of KHC_2O_4. Finish as before.

Weigh out 20 gm. of KHC_2O_4 and 20 gm. of oxalic acid. Dissolve together in 20 c.c. of hot water. Without dissolving all, dust in 10 gm. of potassium dichromate powder gradually. Carbon dioxide is evolved with effervescence, the liquid becoming dark blue with red reflex. Evaporate to crystallisation. Thus $K_3Cr(C_2O_4)_3$ 6 aq.

The solution of the potassium chromium oxalate gives no pp. either for Cr''' or for oxalic, these forming a stable ion, $Cr(C_2O_4)_3'''$.

b. It is removed from its salts by the action of dil. sulphuric on the calcium salt obtained by precipitation from sol. salts (below), or by suspending an insol. salt in water or dil. NH_3.Aq., passing in H_2S, filtering, etc.

c. Salts obtained by precipitation are $CaC_2O_4.H_2O$ and C_2O_4Fe, insol. in dil. acetic.

To a soln. of 10 gm. of the $K_2C_2O_4$ above add dil. acetic, then calcium chloride, warming, to complete precipitation. Filter and wash well with warm dil. acetic. Calculate the amount of dil. H_2SO_4 required for this from the $K_2C_2O_4$. Mix the pp. with this amount of dil. H_2SO_4, warming. Let stand, then filter. Boil the filtrate with a pinch of calcium oxalate. Filter again and evaporate the filtrate to crystallisation.

To a soln. of ferrous sulphate add oxalic soln. A yellow pp. is produced. Compare with this the sol. ferric oxalate, $Fe_2(C_2O_4)_3$, yellow-green transparent flakes, becoming opaque green and often powdery.

DI-HYDROXY-DI-CARBOXY ACIDS.

Tartaric Acid, COOH.CHOH.CHOH.COOH.

The ordinary acid is the dextro form. It is a crystalline solid of definite m.p., readily sol. in water, sol. in alcohol, insol. in ether.

Salts of the alkalis are sol., also a few others, *e.g.* ferrous, ferric.

I. *a*. The acid and its salts burn with a nearly non-luminous flame, evolving a smell of burnt sugar and leaving a large carbon residue containing carbonate if from an alkali metal, and therefore alkaline to litmus.

Heat specimens of acid and of salt as usual. Note the above.

b. Being a hydroxy cpd. it is rather susceptible to wet way oxidation. In most cases the change is complex.

d. Fehling's Soln., of course, is not reduced.

e. Tollens' Reagent gives a silver mirror.

Confirm this.

Hydrogen peroxide in presence of ferrous sulphate, Fenton's Reagent.

Add a little $FeSO_4$ soln. to a soln. of a tartrate, then a little very dil. H_2O_2, and immediately some caustic soda soln.: a violet coloration is produced.

VI. Phosphorus pentachloride causes complete decomposition.

VII. 1. *c*. The OH of the CHOH group can be etherified in two stages.

4. *b*. Similarly, mono- and di-acetyl tartaric esters are easily obtained from acetic anhydride in proper proportions, and *e.g.* ethyl tartrate.

The ordinary carboxy esters are prepared from the acid and alcohols with HCl gas as a dehydrator, removing the water, etc., by distillation in a vacuum.

VIII. Tartaric acid is a fairly strong acid. It and its hydrogen salts can be titrated as di- and mono-basic acids respectively.

In presence of metals of Group III. complex ions are formed in which the metal is part of the — ion, and therefore is not ppd. by the group reagent, ammonia. The Fe''' cpd., however, does give a pp. with Am_2S.

Add ammonia to a soln. of ammonium ferric tartrate: no pp. Pass in H_2S, there is a pp. of black $FeS + S$. See chromoxalates, under Oxalic Acid.

IX. Only the alkyl and acyl derivatives mentioned in VII. can be hydrolysed, each in the appropriate manner.

X. *a*. Cautious dehydration of the acid by direct heating results in the formation of complex anhydrides.

Warm the acid and its salts with conc. H_2SO_4; they char at once.

d. The acid heated with potassium hydrogen sulphate gives pyruvic acid, $CH_3COCOOH$.

XII. *a*. The acid and the hydrogen tartrates easily decompose carbonates.

Weigh out 30 gm. of tartaric acid, dissolve in hot water. Add K_2CO_3 until neutral: thus a soln. of $K_2C_4H_4O_6$. Add another 30 gm. of acid dissolved in hot water. Let cool. Collect the $KHC_4H_4O_6$ formed. Dry at pump, etc.

Weigh out about half the product, dissolve in boiling water, neutralise with $NaHCO_3$. Evaporate down. Let the $NaKC_4H_4O_6.4$ aq. crystallise out.

This is Rochelle Salt.

Weigh out 20 gm. of the rest and dissolve in boiling water. Add 16 gm. of antimonious oxide. This should dissolve, forming Tartar Emetic. Filter if necessary. Evaporate to crystallisation. Filter and dry at the pump. It is $K(SbO)C_4H_4O_6.\frac{1}{2}$ aq.

b. It is removed from its salts in the same manner as oxalic acid.

c. It forms a number of insol. salts.

To a neutral soln. of a salt add $CaCl_2Aq$. (not sulphate). On warming gently a white crystalline pp. of tartrate is obtained, sol. in acetic and in caustic alkalis.

XIII. Tartrates and the acid give condensation products with resorcinol.

Heat gently on a piece of porcelain with a drop or two of conc. sulphuric containing 1 per cent. of resorcinol. A purple red colour is observed.

ACIDS OF OTHER GROUPS.

Of these, that of the *mono-hydroxy-tri-carboxy* is represented by:

Citric Acid, $HOOC.CH_2.C(OH)COOH.CH_2.COOH$.

A crystalline solid $+H_2O$, of definite m.p. Easily sol. in water, sol. in alcohol, sol. with difficulty in ether. Its sol. salts generally contain water of crystallisation, varying in amount.

Use the acid and tri-sodium citrate.

I. *a.* The acid and its salts burn with a luminous flame, leaving much carbon, the alkali salts leaving also carbonate.

Wet way oxidation gives often complex mixtures of substances.

e. Tollens' reagent is reduced, but no mirror is obtained.

Test as for tartrate: black pp. of silver.

VI. Phosphorus halogenides give complete decomposition.

VII. 1. The alcoholic OH group can be etherified.

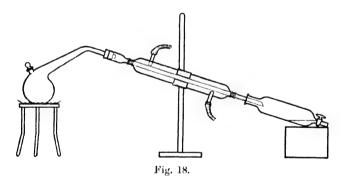
3. This and the three COOH groups can be esterified, there being, of course, three esters according as one, two, or three COOH groups are involved.

4. The OH group can be acylated.

VIII. Citric acid is a strong tribasic acid, forming three sets of alkali, etc., salts, the alkali di-hydrogen and mono-hydrogen salts acting as di- and mono-basic acids. With Group III. metals it behaves as does tartaric acid.

X. *a.* On dehydration by heat, first one molecule of water is eliminated, aconitic acid, $C_6H_6O_6$, being formed. This then loses water and CO_2, giving itaconic anhydride, $C_5H_4O_3$, this passing into citraconic anhydride, isomeric.

†Melt 100 gm. of citric acid in a porcelain basin at 150°, thereby dehydrating it. Break up the fused mass, introduce it into a retort with bent neck fitted to a condenser. Use a tap funnel as receiver. Distil rapidly until the distillate has a brown colour and the residue has charred. The distillate separates into two layers. Separate these and use the upper (water and the acid) for the tests (Fig. 18).

Fig. 18.

Show that it behaves like an unsaturated cpd., decolorises Br.Aq., and easily reduces alkaline $KMnO_4$.

Fit up a vacuum distillation apparatus: a distilling flask fixed to a condenser, the lower end of which is fitted into the neck of another distilling flask as receiver. The side tube of this is connected with one limb of a T-piece in the neck of the pump flask, the other limb being fixed to a manometer. A simple form of this consists of a tube bent with parallel limbs, one limb of which, about 80 cm. long, dips into a dish of mercury. All joints must be as

perfect as possible, and they must be tested by finding the height to which the mercury rises in this tube when the pump is working, the pressure then being the difference between the barometric height for the time of experiment and this height. Unless this pressure is < 100 mm., the joints had better be refitted. Put the original lower layer into the distilling flask, adding pieces of porous pot to prevent "bumping" during this distillation. Use as small a flame as will keep the liquid boiling when close to the flask; b.p. of anhydride 110°-114° at 30 mm See Fig. 6.

d. Another part loses CO, giving acetone-dicarboxylic acid, and this passes into acetone and CO_2, the former being the main result of heating with conc. sulphuric, not too strongly.

Try this reaction; there should not be much blackening.

XII. *a.* The three sets of salts are obtained as usual (see Tartaric Acid).

b. The acid is obtained from its salts as oxalic acid.

c. It forms various insol. salts.

Calcium chloride gives in neutral solns. on boiling a white pp. of tribasic citrate, sol. in acetic, insol. in KOH.

CHAPTER IX.

ACYL DERIVATIVES.

1. Esters RCOOR, etc. Acyl Ethers.

a. Those in which the H of the acid has been completely replaced by alkyl, etc., groups.

These are colourless substances, the physical state of which depends generally to a greater extent on the nature of the basic part, the alcohol, than on that of the acid. Thus the esters of glycerol are solids, while diethyl tartrate is a liquid, but the methyl esters are often solids if the acid be solid. They are easily sol. in alcohol and in organic solvents, also in some cases and to varying extent in water, but insol. in salt solns., and therefore they can be "salted out" by adding *e.g.* $CaCl_2$ or NaCl to the aq. soln.; if liquid and lighter they float as an upper layer. Many of them have characteristic fruity odours. Many distil unchanged, others can be distilled only in a vacuum.

Compare: ethyl acetate and oxalate; methyl oxalate; glyceryl tristearate (tallow); cetyl palmitate (spermaceti).

I. *a.* All are more or less combustible, the nature of the flame and the extent of charring depending on the complexity of composition.

Compare the flames of the above esters by trial.

The results of wet way oxidation in general suggest that hydrolysis had preceded it, but the esters of hydroxy acids might be oxidised without hydrolysis, *e.g.* diethyl tartrate into diketotartrate.

*II. *a.* Hot zinc dust in excess in most cases acts normally, causing complete reduction to the corresponding saturated hydrocarbon, *e.g.* ethyl acetate to normal butane.

By wet way reduction it should be possible to act on reducible groups, *e.g.* aldehydic or ketonic, inside the molecule, without precedent hydrolysis; thus pyruvates might give lactates.

Also the esters of halo-substituted acids might give those of unsubstituted acids, thus ethyl chloracetate might give ethyl acetate.

*V. *a.* Some esters can be directly halogenated, partially or completely, without other change, the halogen attacking mainly the alcohol group.

c. Sodium generally acts peculiarly, producing in the end the sodium cpd. of the enolic[1] form of esters of ketonic acids, *e.g.* ethyl acetate gives sodium ethyl acetoacetate. This does not include a direct replacement by Na, but diethyl malonate gives diethyl disodiomalonate.

*VI. When phosphorus pentachloride does act, it acts as it does on ethers, causing separation into alkyl chloride and acyl chloride.

*VII. Etherification of any alcoholic OH groups left and also esterification of any groups whatever may happen. Thus diethyl tartrate should give mono- and diethoxytartrate and mono- and di-acetyltartrate. This latter is obtained without difficulty with acetic anhydride.

VIII. Esters are not in general ionised, even in alcohol soln., to any great extent, so they do not, without hydrolysis, always give the characteristic reactions either for alcohol or for acid.

Try the effect of ethyl acetate on ferric chloride.

IX. Hydrolysis: the typical reaction for esters.

a. A few esters are hydrolysed easily by cold water, so their aq. solns. are acid and give reactions for the acid.

Dissolve methyl oxalate in water, note acidity of the soln., add calc. chloride and acetic. The usual pp. is produced.

[1] For the explanation of "enolic" see Part II.

b. Generally, however, they require boiling with aq. alkalis.

Measure out 25 c.c. of ethyl acetate into a round-bottomed flask, add 25 gm. of caustic potash in 75 c.c. of water, put in a few pieces of porous pot and boil under a reflux condenser until the upper layer of ester has gone. Turn down the condenser and connect the flask with it by a bent tube. Distil off anything volatile from a water bath. This will contain some unchanged ester. Salt out by adding excess of NaCl and separate. Go on with the distillation over a sand bath until the temperature reaches 100°. Mix the distillate with the residue from the first separation, salt out the alcohol with dry K_2CO_3; separate. Identify the ethyl alcohol. Neutralise the alkaline residue with dil. H_2SO_4, evaporate to dryness on the sand bath, break up the residue, add 20 c.c. of conc. H_2SO_4 and distil with thermometer from a small flask, collecting up to 130°. Redistil the acetic acid over a little dry fused sodium acetate.

c. Dil. acids are used similarly, best H_2SO_4. In this case, alcohol and organic acid are set free and may be tedious to separate.

d. Heating with soda lime may have the same effect, but see X. *d.*

X. **a.* Elimination of water may be caused by hot conc. H_2SO_4 as usual. This in most cases causes the destruction of the molecules, but esters of hydroxy-acids might give esters of unsaturated acids.

**b.* Alcoholic KOH might similarly cause elimination of HX from esters of halosubstituted acids, thus brompropionate might give acrylate. But in most cases alcoholic KOH would cause hydrolysis; indeed, it has to be used when the ester is too insol. in aq. KOH, and hydrolysis with that fails. Thus ethyl brompropionate might give potassium bromide and acrylate and ethyl alcohol.

See hydrolysis of tallow in the preparation of Stearic Acid.

d. Removal of CO_2 by hot soda lime should give corresponding hydrocarbon, but of course hydrolysis also happens—at any rate, at first.

With ammonia gas or its conc. soln. in water or in alcohol, esters give acylamides, if insol. as a pp.

Mix ethyl oxalate with conc. NH_3Aq, a white pp. of oxamide is formed.

*XIII. Some of the normal esters react with ethoxide, etc., forming so-called "ortho-esters." Thus ethyl acetate adds on sod. ethoxide, forming sodium diethyl orthoacetate, the first step in the synthesis of ethyl acetoacetate. Then may follow a condensation with another mol. of the same or of a different ester, with the elimination of ROH, producing a more complex cpd. Thus the above, with another mol. of EtOAc, gives the Na cpd. of ethyl acetoacetate, EtOH being eliminated.

XIV. Esters of aldehydic and ketonic acids give most of ordinary aldehyde and ketone reactions, *e.g.* pyruvates, glyoxylates, acetoacetates react with H_2NOH and $PhNHNH_2$, generally normally.

*β. These in which the H of the COOH groups has not been completely replaced by alkyl, etc., groups, *i.e.* acid esters, *e.g.* HOOC,COOEt, monethyl oxalate.

These generally behave normally, but :—

VIII. They are generally sol. in water, and ionised so that the substance is an acid as well as an ester (compare ethylsulphates), having H ions and a new negative ion containing the alkyl, not having the same reactions as the original negative ion of the acid.

Compare ethylsulphates with sulphates; ethyloxalates with oxalates.

XII. These esteracids show many of the properties of acids, forming salts unlike those of the parent acid in solubility and reactions.

2. Acyl Halogenides, *e.g.* RCOCl, etc.

These are colourless liquids, heavier than water, often with a characteristic odour (but see IX. below), distilling unchanged at atmospheric pressure, often miscible with organic solvents, even when there is no mutual action.

Use *Acetyl Chloride*, note above points, and its solubility in benzene.

I. *a.* Generally incombustible, or nearly so, cp. alkyl haloid esters.

Try as usual.

VII. 4. *a.* With alcohols and alkylates, they give esters and halogen hydride or its salt, seldom haloid ester and acid.

Put a few drops acetyl chloride into excess of EtOH in a t.t. Note smell of ethyl acetate. Add some $CaCl_2$, the ester separates as an upper layer. Repeat with sod. ethoxide, cooling well; sodium chloride is ppd.

With salts of fatty acids, acid anhydrides are produced, which may be "mixed," *i.e.* contain two different acyl groups.

See Preparation of Acetic Anhydride.

IX. The group reaction: hydrolysis.

a. By water: a rather violent reaction with lower members: into organic acid and halogen hydride. The lower members are hydrolysed by atmospheric moisture, so fume in air, giving a mixed smell of the two products.

Note these properties in the case given.

b. Alkalis at once give salts of the organic acid and of the halogen acid, often violently.

Add a little to caustic soda; identify the products.

With NH_3 they give acylamides and ammonium halogen salts.

XIII. *k*. With aromatic hydrocarbons and $AlCl_3$, they give aromatic alkyl ketones and HCl. Thus CH_3COCl and C_6H_6 give acetophenone, $CH_3COC_6H_5$.

**Formyl Chloride*, HCOCl, is unknown, and *Oxalyl Chloride*, $(COCl)_2$, nearly so, the type method of formation resulting in the production of HCl and CO, and of HCl, CO, and CO_2 gases respectively, by dehydration.

Carbonyl Chloride, $COCl_2$, is a colourless gas, of unpleasant smell, fuming in air. Its soln. in dry toluene is much used (as in the synthesis of complex keto-derivatives) in place of the gas itself. It gives, of course, HCl and H_2CO_3, *i.e.* CO_2 and H_2O.

**Malonyl Chloride*, $CH_2(COCl)_2$, behaves normally.

**Succinyl Chloride* reacts on reduction, etc., as if it had the unsymmetrical structure $\begin{matrix} CH_2.CCl_2 \\ CH_2.CO \end{matrix} > O$ instead of the symmetrical $(CH_2)_2(COCl)_2$.

The acid halogenides of the more complex, *e.g.* hydroxy acids, are unimportant.

3. Acyl Anhydrides, RCO.O.OCR.

Those from monocarboxy acids are colourless liquids, heavier than water, generally distilling unchanged at atmospheric pressure, but mixed anhydrides may re-arrange themselves during distillation. Those from dicarboxy acids are often solids and generally more stable than the acids from which they come (by heat dehydration) as they have a definite m.p. and distil unchanged at atmospheric pressure. Some of the anhydrides have a smell distinct from that of the acid, and they are sol. in organic solvents whether they act on them or not.

Use *Acetic Anhydride*. Note the above points.

I. Combustible: more so than the acids generally.
Try with acetic anhydride.

VI. With phosphorus pentachloride they give acid chlorides; compare Ethers.

VII. 3. With alcohols they give esters and acid.

Repeat experiments given under acetyl chloride VII.

On this is founded a method for determining the number of HO groups in an alcohol, or the number of NH_2 or NH groups in an amine, primary or secondary, by estimating, by titration generally, the difference between the amounts of acid, *e.g.* acetic, which a given sample of anhydride, *e.g.* acetic, would give with water only, and with the alcohol, etc.

Every gram-molecule of acid fewer means one OH, NH_2, NH, in the alcohol, or primary or secondary amine. See Sugars, under Glucose.

XI. *a*. Hydrolysis by water: less violent than for acyl haloids: slowly by atmospheric moisture.

b. Hydrolysis by alkalis: as for acyl haloids, but they give salt of organic acid only, of course.

Repeat experiments given under acetyl chloride.

With ammonia gas they slowly give amides and ammonium salt.

4. Acyl Amides, $RCONH_2$, etc.

These are crystalline solids (formamide a liquid) often deliquescent, often with characteristic smell (? due to impurity) with definite m.p., sometimes distilling unchanged (formamide goes into CO and NH_3 largely). The lower members dissolve in water, and nearly all dissolve in some organic solvent.

Use *Acetamide* as type. Its mousy smell is due to an impurity.

I. *a*. Amides are not in general very combustible unless of high molecular weight.

Try acetamide: it is hardly combustible at all.

V. *a*. Halogens, *e.g.* bromine, replace the H of the NH_2 group giving, *e.g.*, mono-bromamides. These on hydrolysis lose HBr and undergo a peculiar change, whereby isocyanic esters are formed. These with excess of alkali give primary amines. See the Preparation of Methylamine from Acetamide.

VI. Phosphorus pentachloride gives chlorimides, by replacing OH in the enolic[1] form, RC(OH)NH, by Cl—thus RCCl(NH).

VII. 2. Ethers of the amides can be obtained by alkylation in the usual way.

4. Di- or tri-acyl cpds. can be obtained by prolonged acylation.

VIII. The solns. of those that dissolve in water show no sign of ionisation, but partial hydrolysis may set in.

IX. Hydrolysis: the characteristic reaction.

a. By water: very slow: giving ammonium salt.

b. By alkalis on boiling, into ammonia and salt of the acid.

Boil a little acetamide with caustic soda, note ammonia evolved, identify the acetate left.

c. By acids on boiling: into free acid and ammonium salt.

Boil a little acetamide with dil. H_2SO_4, note smell of acetic acid.

X. *a.* Amides heated with phosphorus pentoxide give nitriles; thus acetamide gives acetonitrile, methyl cyanide, CH_3CN.

XI. Amides show some signs of basic function, reacting in ether soln. with HCl gas to form salts, insol. in the ether, hydrolysed by water.

XII. They also show acid reactions in their enolic[1] form. Thus acetamide soln. dissolves HgO, forming $(CH_3CONH)_2Hg$.

XIII. *c.* With nitrous acid they give the usual reaction for aliphatic NH_2 cpds., *i.e.* replacement of the NH_2 group by OH, forming acids and N_2.

Add to a little acetamide $NaNO_2$ and dil. H_2SO_4.

[1] For the explanation of "enolic" see Part II.

Urea, $CO(NH_2)_2$, diamide of Carbonic Acid.

A colourless crystalline solid, of definite m.p., sol. in water and in alcohols, hardly sol. in ether. Its salts are crystalline solids of varying solubility, largely hydrolysed by water.

I. *a.* It is not combustible, nor does it alter in air.

k. It is oxidised by bleaching powder or hypobromite into CO_2 (absorbed), water, and N_2 (evolved): on this reaction is based a method for its determination, the N_2 being measured. There is a constant error of 8 per cent., about. Cyanate is also formed.

Dissolve some in water, add NaOH and Br.Aq.

VI. Phosphorus pentachloride causes complete decomposition.

VIII. Its aqueous soln. shows no sign of ionisation.

IX. Hydrolysis, *a.* by water, very slow; *b.* by alkalis, on boiling; *c.* by acids.

Try *b.* and *c.* as for acetamide. Identify NH_3 and CO_2, respectively.

X. *e.* When heated by itself slightly above its melting-point, ammonia is evolved and biuret (allophanamide $H_2NCO.NH.CONH_2$) is formed. This gives a colour reaction with copper salts. This "biuret" is a decomposition product also of more complex nitrogenous bodies, the proteins: so that these also give the test.

Heat a quantity of urea in a t.t. until NH_3 is evolved freely. Then let cool. Add a little water, then a few drops of $CuSO_4$Aq., then NaOH drop by drop: a red to violet coloration appears.

XI. *a.* Urea acts as a monoacid base, combining readily with strong acids. Some of these salts are rather insol. in their own acids, so can be ppd.

Make a fairly conc. cold soln. of urea, add conc. nitric; a crystalline pp. is produced. Less conc. solns. give platy crystals on standing.

Repeat experiment with oxalic acid, a similar result is obtained.

Filter off, wash, and dry a portion of these. Dissolve the specimens in much water. Test the solns. with litmus—strongly acid. See above.

b. The urea can be removed (*α*) from the nitrate by neutralising with K_2CO_3, (*β*) from the oxalate by adding lime water or $CaCO_3$ paste, and filtering; extracting the urea in each case by amyl alcohol.

Carry out this operation in the case of the nitrate.

XIII. *c.* Nitrous acid gives nitrogen, carbon dioxide, and water.

Test as acetamide. Identify products as far as possible.

Oxamide, diamide of Oxalic Acid, $H_2NCO.CONH_2$.

This is a white microcrystalline powder, insol. in water and all ordinary solvents.[1] On heating, it sublimes with partial decomposition.

I. *a.* It is hardly combustible, but the CO formed on heating burns with the usual flame. Little or no carbon residue is left.

Confirm this.

IX. *a.* Hydrolysed by water extremely slowly.

b. Alkalis on boiling give oxalate and ammonia.

c. Dil. acids on boiling give oxalic acid and ammonium salt.

Use for *b.* caustic soda and for *c.* dil. sulphuric Identify the products.

X. *a.* Elimination of water by heating with phosphoric anhydride gives cyanogen gas. Conc. hot sulphuric gives carbon monoxide and dioxide.

Try this latter and identify the products.

[1] Oxamide may be obtained in obvious crystals from boiling dimethylaniline.

Oxamic Acid and its **Esters,** $H_2NCO.COOH$, etc.

The acid is a colourless crystalline solid melting with decomposition, difficultly sol. in cold water. The ethyl ester, oxamethane, crystallises in plates of definite m.p. There do not appear to be any metallic salts.

Both give normal reactions, *i.e.* those to be expected from their nature.

Thus on hydrolysis the acid gives oxalate and NH_3, or oxalic acid and NH_4 salt, with an alcohol in addition from the ester.

With hot conc. sulphuric both behave normally.

> Show that oxamethane gives oxalate, ammonia, and alcohol by hydrolysis.

Carbamic Acid and the **Urethanes,** NH_2COOH, NH_2COOR.

This is the first member of the group, and, like other first members, its properties are rather aberrant, resembling more those of an amide.

The acid is unstable, decomposing when set free from cpds. into CO_2 and NH_3. Nor are the salts well defined cpds., passing readily, by hydrolysis (absorption of water), into carbonates.

The Esters, called Urethanes, are known, and are stable, colourless solids, of definite m.p. and b.p.

Hydrolysis is, of course, the most important reaction, boiling dil. acids giving alcohol, CO_2 and NH_4 salt; alkalis similarly give alcohol, NH_3, and carbonate.

The results of oxidation (aldehydes, etc.) suggest precedent hydrolysis.

Soda lime may remove CO_2 only, leaving primary amine.

> Try Hydrolysis by dil. H_2SO_4 and by dil. NaOH, identifying the products.

***Aminoacetic Acid, Glycin,** $CH_2NH_2,COOH$.

This is the second member of the group, but, of course, has not the structure of an amide.

This is a stable cpd. crystallising in colourless prisms, of sweet taste, decomposing a little above its m.p., sol. in water and in alcohol but not in ether. Its salts with the heavy metals seem

to be formed by replacing one H in the NH_2 group, while those with alkalis are hardly definite cpds. The esters, however, have the normal structure and these and the acid form salts with acids as being amines. The acid combines with salts, *e.g.* with KNO_3, this and other properties suggesting that the free acid is a closed ring.

$$\begin{array}{ccc} CH_2 - NH_3 & CH_2 - NH_2cu^1 & CH_2NH_3NO_3 \\ | \quad\quad | & | \quad\quad | & | \\ CO - O & CO - O & COOK \end{array}$$

It is not easily hydrolysed, but on heating with baryta it loses CO_2, giving CH_3NH_2.

With $FeCl_3$ it gives an intense red colour.

The acid is neutral to indicators; its salts with acids — strongly acid.

With alcohol and HCl gas the HCl salt of aminoacetic ethyl ester is formed, CH_2NH_2COOEt, HCl.

Of the higher amino acids, those with the NH_2 in the α position are of extreme importance in Physiological Chemistry, being degradation products of the proteins, *e.g.* α-aminopropionic $CH_3,CHNH_2,COOH$, alanine.

5. Ureïdes.

These compounds bear the same relation to urea and acids that amides do to ammonia and acids, *i.e.* the compounds are in each case condensation products.

The most important is the di-ureïde of an unknown acid :—

Uric Acid, $C_5H_4N_4O_3$.

This is a microcrystalline powder, generally faintly yellowish. It is insol. in cold water, very slightly in boiling water, insol. in alcohol and in ether. Its salts are rather more sol., especially the dibasic ones.

[1] The symbol "cu" means "half an atom" of divalent copper and is used only for the sake of simplicity in the formula.

I. *a*. The acid is hardly combustible, decomposing into cyanuric and hydrocyanic acids and ammonia, with charring. The salts leave an alkaline residue.

Try the acid in this manner.

d. Fehling's Soln. is reduced on boiling.

e. Tollens' Reagent is also reduced, giving a black pp. of silver.

Confirm these statements.

VIII. The dibasic salts are hydrolysed so that their solns. show an alkaline reaction. The monoacid salts seem to be ionised normally.

IX. *b*. The acid is not hydrolysed by conc. alkalis.

e. Potash fusion gives ammonia and cyanide.
Try this.

X. The acid dissolves in cold conc. sulphuric, but is reppd. by water. On heating, the soln. is charred.

XII. *a*. The acid is dibasic, forming two series of alkali salts. It therefore dissolves in alkalis, and in their alkaline salts, forming dibasic and monobasic salts respectively.

b. Mineral acids pp. the acid again.

Dissolve some uric acid in caustic soda; divide into two parts. To one add dil. sulphuric acid; uric acid is ppd.; add to this borax soln. until the pp. dissolves. Pass carbon dioxide through the other, the acid salt, *i.e.* hydrogen sodium urate, is ppd.

Uric acid shows the Murexide Reaction. Evaporate a little with conc. nitric in a porcelain dish to dryness over a water bath; a yellow, reddish brown, or magenta-coloured residue remains, according to the time of heating. Let cool, add a drop of $NH_3Aq.$; the colour becomes violet: add then a drop of NaOH; the colour becomes blue.

6. Cyanogen Compounds.

Hydrocyanic Acid and **Cyanides.**

The acid is a colourless liquid, very volatile, lighter than and miscible with water, forming the ordinary soln. called "prussic acid." It has a peculiar odour and it and its salts are very poisonous. Metallic simple cyanides are often well-defined salts. Those of the alkalis are sol. in water, less sol. in alcohol, smelling like the acid. See IX.

Use *Potassium Cyanide; Mercury Cyanide.*

I. *a.* The real acid burns with a characteristic purplish flame, into water, CO_2, and nitrogen.

Add some dil. H_2SO_4 to a little good KCN (solid) in a t.t. Note cautiously the smell of the acid—apply a light to t.t.

The salts are hardly combustible, but some decompose giving cyanogen gas which burns like the acid.

† Heat a very little mercuric cyanide in an ignition tube. Note flame of C_2N_2 and mirror of mercury.

b. Dry alkali cyanides heated with oxidising agents, *e.g.* red lead, or $K_2Cr_2O_7$, give Cyanates.

See Preparation of Urea.

II. Nascent hydrogen reduces the acid to methylamine by addition.

III. The acid may be considered as an unsaturated cpd. since it combines directly with halogen hydrides. See also II.

The salts have a great tendency to form "double cyanides" of varying resistance to reagents. See XII.

V. *c.* Sodium replaces hydrogen of the acid, forming salts.

VII. 3. *a.* Esters are not made directly from the acid.

b. By heating dry KCN with dry alkylsulphates, alkyl cyanides are made.

c. By heating silver cyanide with alkyl iodides alkyl isocyanides are obtained.

VIII. The acid in soln. is very weak, *i.e.* very incompletely ionised and:—

IX. *a.* The alkali salts are largely hydrolysed in soln.; hence they smell of the acid and are strongly alkaline. Mercury cyanide has no smell and it is only very slightly ionised.

Confirm these statements.

c. By boiling the acid or its alkali salts with dil. acids, hydrolysis into formic acid and NH_4 salt is caused, hence the name "Formonitrile."

e. Potash fusion or soda-lime causes evolution of NH_3.

Mix well some KCN with soda-lime, heat strongly; identify NH_3.

X. *a.* With medium conc. H_2SO_4, hydrolysis and dehydration proceed together, *i.e.* CO is evolved.

Try with KCN, $HgCy_2$.

XII. *a.* The acid reacts with bases forming salts.

b. It is removed from its salts by dil. mineral acids—generally.

Try KCN and dil. H_2SO_4; HCN evolved.

Try $HgCy_2$ and dil. H_2SO_4; no result. See IX. *a.*

c. Insol. salts are formed by pptn. These dissolve in excess of KCN.

Add KCN soln. to $AgNO_3$ soln. White pp., sol. in excess of KCN.

Mix KCN and $CuSO_4$ solns. boiling; there is an attempt at a pptn., which gives place to a clear liquid evolving C_2N_2 gas; identify by applying a light. The soln. contains a sol. cuprocyanide.

The solns. contain sol., more or less stable, double salts.

Add HNO_3 dil. to the Ag soln., (above) AgCN reformed.

In some cases, however, the heavy metal forms a stable complex metallocyanogen ion.

Add KCN to $FeSO_4$ soln. and boil, thus forming potassium ferrocyanide. Then to part, add $FeCl_3$ soln.; a deep blue pp. of ferric ferrocyanide "Prussian Blue" is formed. To the other part, add $CuSO_4$ soln.; a brown pp. of copper ferrocyanide is formed. Repeat the experiment, using $FeCl_3$ at first, forming ferricyanide, and then $FeSO_4$; a deep blue pp. of "Turnbull's Blue" is obtained. Add dil. HCl to these three. There is no change.

Put some KCN solid into a beaker; add dil. H_2SO_4 and cover the beaker at once with a watch glass on the under side of which hangs a drop of yellow ammonium sulphide. Warm the beaker gently until all HCN is driven off. Some collects in the drop, forming ammonium thiocyanate. Evaporate the drop to perfect dryness. Then touch the spot with a drop of $FeCl_3$ soln. The dark red colour of ferric thiocyanate is shown.

Cyanogen Esters.

These esters differ from esters of the COOH acids in the peculiar results they give on hydrolysis, not alcohol and acid, or salt of it, as usual.

There are two groups, differing in structure, as shown by their hydrolysis products (and otherwise) —

a. True Cyanides, of form RCN.

Hydrolysis products RCOOH and NH_3; hence called also *acid Nitriles*.

These are colourless liquids, only slightly sol. in water and of not unpleasant smell, boiling unchanged under atmospheric pressure.

I. *a*. Readily combustible.

II. *b*. Nascent hydrogen (Na and (amyl) alcohol) converts them into the next higher primary amine. Acetonitrile or methyl cyanide gives ethylamine.

III. *b*. Like the acid, they behave as unsaturated bodies.

d. Addition of water probably precedes hydrolysis as usual, amides being formed first probably.

IX. *a.* Water, even boiling, hydrolyses them very slowly.

b. Boiling dilute alkalis }
c. Boiling dilute acids } do so more readily, forming :—

b. Ammonia and salt of fatty acid }
c. Ammonia salt and free fatty acid } hence their structure.

β. Isocyanides of form RNC.

Hydrolysis products primary amine and formic acid.

These are liquids, often bluish, with a most unpleasant generic odour; they have a lower b.p. than normal cyanides, into which they pass partially at temperatures above their b.p.

I. *a.* Less combustible than true cyanides.

III. They also react as unsaturated bodies. See Nitriles.

IX. *b.* From their mode of preparation it is obvious they cannot be hydrolysed by alkalis, but :—

c. Conc. mineral acids convert them into primary amine (salt) and free formic acid.

Boil the "remains" of an "Isocyanide Test" with conc. HCl in a t.t. The smell disappears.

It is doubtful whether these differences occur in HCN itself or in the metallic cyanides, but KCN with alkyl derivatives gives nitriles; silver cyanide gives isocyanides.

Cyanates.

The acid is a sharp-smelling, colourless liquid, stable only in a freezing mixture, decomposing at ordinary temperature into CO_2, ammonia and cyanuric acid ($H_3C_3N_3O_3$), etc.

Two structures are possible for salts and esters, but it is not definitely determined to which structure known salts are to be referred, nor is it certain that both forms have examples. Only isocyanic esters are known.

The salts are crystalline sol. solids, or pps., often decomposed by acid.

Use *Potassium Cyanate.*

I. *a*. They are not combustible, nor easily decomposed by heat, if dry.

Try as usual.

II. They cannot be directly reduced.

VII. Esters (isocyanic) can be obtained in the usual way.

VIII. Soluble salts are in general fairly completely ionised, and also to some extent hydrolysed, showing an alkaline reaction.

XI. The acid hydrolyses in part as soon as set free, as above. The salts are hydrolysed by boiling with the usual reagents *b*, *c*, *e*, into ammonia and carbonate or NH_4 salt and CO_2.

Try these reagents on potassium cyanate. Note results.

X. Conc. H_2SO_4 gives the same results as hydrolysis.

XII. *b*. Even dil. mineral acids set free the acid, decomposing as above.

c. Preparation of insoluble salts.

With $AgNO_3$ a white pp. of Ag. isocyanate is formed. It dissolves in NH_3 Aq., like most silver salts.

On boiling this with alkyl iodides, alkyl isocyanates (*q. v.*) are formed.

Ammonium cyanate in aq. or alcoholic soln. passes on warming into urea, isomeric, probably by successive dehydration and rehydration.

Mix 10 gm. of potassium cyanate with 17 gm. of ammonium sulphate and 50 c.c. of alcohol; warm together for some time. Filter off the ppd. K_2SO_4 and evaporate the filtrate to crystallisation. Identify the crystals as urea.

**Isocyanic Esters*, of form RNCO.

These are colourless liquids, of tear-exciting odour, distilling unchanged. They are known to have the iso form, from their hydrolysis into primary amines and carbonates.

Thiocyanic Acid and Salts, HSCN, etc.

Here again two structural forms are possible, but it is not known definitely to which form the acid and salts should be referred. See Esters VII. 3. *b*.

The real acid is a colourless sharp-smelling liquid nearly as unstable as cyanic acid. Dil. solns. are fairly stable but cannot be concentrated. The sol. salts are colourless, etc., crystalline solids often deliquescent and sol. in alcohol—NH_4, Na, K—or insol. pps. Cu, Ag, Hg—often sol. in excess of salt of alkali.

I. *a*. As containing sulphur, these cpds. are combustible. The combustion of $Hg(SCN)_2$ gives a serpentiform ash, "Pharaoh's serpents."

Peculiar complex coloured bodies are obtained by oxidation.

VII. 3. *b*. True thiocyanic esters are obtained by distilling alkylsulphates or alkyl iodides with KSCN, but silver thiocyanate appears to give iso-thiocyanic esters, the "mustard oils."

VIII. In dil. soln. the acid is fairly well ionised. The sol. salts are also well ionised.

IX. *b*. The salts are not hydrolysed by alkalis but:—

c. Conc. acids give HSCN which then decomposes into COS (carbonyl sulphide), H_2S, CO_2, etc., and NH_4 salt.

Treat a small quantity of KSCN with cold conc. HCl. Note result. Then warm. Note result. Try similarly, cold and hot conc. H_2SO_4. SO_2 also is produced here of course.

d. Potash fusion and sodium fusion give sulphide and cyanide, etc.

XII. *a*. The dil. acid neutralises alkalis and attacks carbonates.

c. *α*. Silver nitrate gives a white pp. of AgNCS, soluble in ammonia.

β. Ferric chloride gives a deep red, almost opaque coloration, due to formation of a soluble double cpd., soluble in alcohol and ether. The colour is not destroyed by dil. HCl.

Confirm *c*, *α* and *β*.

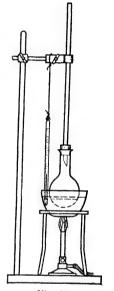
XV. The acid tends to polymerise into cyanuric form.

Ammonium thiocyanate, on heating, passes largely, but not completely, into thiourea. Further heating gives guanidine, $NH_2C(NH)NH_2$, as thiocyanate.

Heat 50 gm. of dried NH_4SCN in a round-bottomed flask on oil bath at 140°-150° for 5-6 hours. Cool, powder and grind up with 25 c.c. of cold water. This dissolves any NH_4SCN left. The residue is recrystallised from hot water.

Fig. 19.

*** Thiourea,** NH_2CSNH_2.

When pure, this crystallises in prisms, impure specimens in silky needles. It has a definite m.p. and dissolves in water and in alcohol, not in ether. It is a weak base, forming salts with strong acids, and, like other amides, it reacts with bases to form salts, in its enolic form.

Hydrolysis with alkalis or with acids decomposes it normally into H_2S, ammonia and CO_2, these reacting further with the alkali or acid.

Heated with water, it passes back into ammonium thiocyanate.

HgO and water on heating produce cyanamide NH_2CN.

Prove that Thiourea contains sulphur.

AROMATIC GROUP.

CHAPTER X.

HYDROCARBONS.

Benzene and its Homologues.

These are colourless liquids with characteristic smell, boiling unchanged at atmospheric pressure, insol. in water and aq. solns., sol. in organic solvents.

Use *Benzene, Toluene* and commercial *Xylene.*

1. *a.* All are highly combustible, burning with smoky flame.

Try this as usual.

To wet way oxidation they are more susceptible than the paraffins, except benzene, which resists pretty well.

b. Acid dichromate slowly burns them to carbon dioxide and water.

c. Alkaline permanganate oxidises alkylbenzenes to acids, the side chains passing into COOH, generally completely, no matter how long.

Heat on a sand bath 10 c.c. of toluene with excess of alkaline $KMnO_4$ in a small flask under a reflux condenser, for an hour. Pour off into a basin and boil off any unchanged toluene over a sand bath. Then clear the mixture and pp. the benzoic acid by passing in sulphur dioxide, cooling. Thus crystalline flakes of the acid are obtained.

The xylenes give the isomeric phthalic acids. Ethylbenzene should give alphatoluic acid—phenylacetic—but benzoic generally results.

g. Dil. HNO_3 oxidises these, with results generally similar to those above.

l. Toluene with chromyl chloride gives a brown pp. of addition product, this with water gives benzaldehyde.

II. Reduction is addition of hydrogen; this is not an easy operation.

f. Nascent hydrogen (from Na and alcohol) gives di-, tetra-, and hexa-hydro derivatives, the last being saturated cyclic hydrocarbons.

j. Hot conc. HI in a sealed tube gives hexahydro derivatives as above.

III. In general they react as saturated cpds., but in sunlight in the cold, chlorine gives addition products, like benzene hexachloride, $C_6H_6Cl_6$. See Ethyl Benzene.

V. *a*. Replacement by halogens happens more easily than in the paraffins.

See Preparation of Brombenzene.

c. Sodium has no action on these hydrocarbons.

XIII. *a*. Sulphonation, by conc. sulphuric acid.

See Preparation of Potassium Benzenesulphonate.

Boil with shaking, 5 c.c. of benzene and 10 c.c. of conc. H_2SO_4 in a small flask under a reflux, on sand bath, until the benzene has almost gone. Pour into 20 c.c. of water. Add a conc. soln. of NaCl. $C_6H_5SO_3Na$ crystallises out.

b. Nitration by conc. nitric with conc. sulphuric.

See Preparations of Nitrobenzene and di-Nitrobenzene.

Mix 2 c.c. of benzene with 5 c.c. of conc. nitric acid and 5 c.c. conc. sulphuric acid in a t.t., warm in water bath. Pour into water. Note smell of nitro cpd.

k. Aluminium Chloride Condensation, the Friedel-Crafts Reaction.

When heated with $AlCl_3$ and halogen cpd., HCl is eliminated and a substituted aryl cpd. results.

See Preparations of Diphenylmethane, Triphenylmethane, Acetophenone, etc.

Aromatic-Aliphatic Hydrocarbons.

The aliphatic part in these is described as the "side chain" or "chains," as distinct from the closed chain or ring nucleus.

a. Those with saturated side chains.

They show the properties, more or less, of both groups of hydrocarbons. Thus as ring cpds. they can be nitrated and sulphonated, and they undergo condensations with $AlCl_3$; and as aliphatic radicals, the side chains are rather more easily oxidised than the ring part is, in general.

Toluene, methyl benzene, the *Xylenes*, dimethyl benzenes *o*, *m*, *p*, have been described with Benzene.

**Ethyl benzene* is a colourless liquid of definite b.p., burning with a smoky flame. Oxidation should give phenylacetic acid $PhCH_2COOH$, but benzoic is generally the only recognisable product. When halogens act on the boiling hydrocarbon they enter the side chain; thus $PhCH_2CH_2Cl$ and $PhCH_2Cl$ from Toluene. But at ordinary temperature, with a carrier, the halogen enters the ring; thus $ClC_6H_4C_2H_5$ and $ClC_6H_4CH_3$ from Toluene.

Nitration and sulphonation take place on the ring.

* *Diphenylmethane*, Ph_2CH_2, is a colourless solid, with sweet smell, volatile unchanged, oxidised by chromic acid to benzophenone, and giving with Br_2, Ph_2CHBr, whence by hydrolysis Benzhydrol Ph_2CHOH is obtained: also obtained by reduction of benzophenone. Further reduction gives Ph_2CH_2 again.

* *Triphenylmethane*, Ph_3CH, is a colourless solid, volatile unchanged. It crystallises from benzene with benzene of crystallisation (one molecule). Oxidation gives triphenylcarbinol Ph_3COH which behaves like a base, forming salts which are ionised in soln., *e.g.* Ph_3CCl.

* *Dibenzyl*, $PhCH_2CH_2Ph$, a colourless solid volatile unchanged, is oxidised to benzoic acid by $K_2Cr_2O_7$ and acid, or alkaline $KMnO_4$, and otherwise it behaves like diphenylmethane.

**β*. Those with unsaturated side chains.

Ph-Ethylene, mono, $PhCH:CH_2$ *Styrolene*.

Ph-Acetylene, mono, $PhC:CH$.

These show the usual reactions for unsaturated cpds. Thus they add on—

Br_2 or HI, $HSO_4.H$ or H_2 nascent.	$2Br_2$, 2HI, etc., in two stages forming ethylbenzene or its 1, 2 derivatives, etc.

They are easily oxidised by alkaline permanganate into glycols, etc.

This does not react with Na, nor form any cuprous or Ag derivatives.	With Na this gives PhC : CNa, also forms cuprous and Ag derivatives.
Di-Ph-Ethylene, PhCH:CHPh is *Stilbene*. It reacts similarly to the above.	*Di-Ph-Acetylene*, PhC : CPh is *Tolane*. Forms no cuprous or Ag derivatives.

Complex Rings.

Naphthalene, $C_{10}H_8$, *i.e.*

This is a colourless solid, crystallising in plates, like many other organic substances, of definite m.p. and b.p., with peculiar smell. It is insol. in water and aq. solns., sol. in organic solvents.

I. *a*. It is combustible and burns with a very smoky flame.

Confirm this by heating it on a piece of porcelain.

Wet way oxidation, various methods give various products.

c. Alkaline permanganate gives (ortho) phthalic acid.

Try with $KMnO_4$. This requires long boiling.

l. Chromic anhydride in glacial acetic, boiling, gives *a*-naphthoquinone.

II. Reduction. Nascent hydrogen gives various di- . . . . octo-hydro-derivatives.

III. Addition cpds. are formed. Thus nascent chlorine, *i.e.* $KClO_3$ and HCl, gives a tetrachloride, $C_{10}H_8Cl_4$, from which, by oxidation, phthalic acid is often prepared. See this Preparation.

V. *a.* Halogens do generally substitute, however.

XIII. *a.* Sulphonation proceeds as usual.

Mix 50 gm. of naphthalene with 60 gm. of conc. sulphuric in a quarter-litre flask fitted with a long wide tube as air condenser. Heat on the oil bath to 170°-180° for four to five hours. Pour the liquid into a litre of water. Boil and neutralise with slaked lime. Filter hot through calico, squeeze out and wash the residue with hot water. Evaporate down until a sample crystallises on cooling. Let cool and finish the preparation as usual. See Fig. 19 for apparatus.

b. Nitration also as usual, but the first stage is the *α*-cpd., the *β*-cpd. having to be obtained by complex processes, from *β*-derivatives.

k. Naphthalene gives the usual condensations with $AlCl_3$.

Naphthalene mono derivatives exist in two forms, *α* and *β*

Anthracene, $C_{14}H_{10}$.

Commercial specimens are yellow crystalline powders; when pure, colourless tables with blue fluorescence. Easily sol. in hot benzene, less so in alcohol and in ether, sol. in other organic solvents.

Phenanthrene, $C_{14}H_{10}$.

Commercial specimens are yellow powders; when pure, colourless plates. Solns. show a blue fluorescence. Easly sol. in ether and in benzene, less so in alcohol, sol. in other org. solvents.

Both have definite m.ps. and b.ps. They react quite like naphthalene.

I. *l.* CrO_3 in glacial acetic gives quinones (*q.v.*).

CHAPTER XI.

HALOGEN COMPOUNDS.

Aryl Halides, Arylene Dihalides.

In the cpds. to be described now, the halogen is attached to the ring. Those in which the halogen is attached to the side chain are described in Chapter XVIII.

These are liquids or solids, with smell, pleasant generally, with definite m.p., and distilling unchanged under atmospheric pressure. They are insol. in water and aq. solns., sol. in organic solvents.

In these, the character of esters shown by aliphatic halides has gone, and they form the best example of replacement by halogen without much change in properties. See the aliphatic halides.

Use *Mono-brombenzene* and *p-di-brombenzene.*

I. *a.* They are combustible, burning with usual smoky flame.

Try with the above as usual.

Results of wet way oxidation similar to those for corresponding hydrocarbon.

c. Alkaline permanganate converts alkylbenzene halides into halo-benzoic acids just as alkylbenzenes similarly give benzoic acid.

II. *f.* Nascent hydrogen, *e.g.* Na and alcohol removes the halogen, but not very rapidly, and it may also partly hydrogenise the ring (see Hydrocarbons II.). This is almost the only way in which halogen can be removed from the ring.

Mix brombenzene with alcohol. Add sodium. Identify the Br as usual.

V. *a.* Halogens continue the replacement: a little p-dibrombenzene is generally obtained in the preparation of monobrombenzene. See below VII., IX.

VII. 1. Etherification with alkylate or with arylate is almost impossible.

3. Similarly, esterification with silver salts is very difficult.

Polyhaloid cpds. react more easily in these cases.

VIII. They are not ionised, not even in alcoholic soln.

Test phenyl bromide in alcohol with alcoholic silver nitrate.

IX. The monohalides are not esters, because they do not hydrolyse.

Try phenyl bromide with alcoholic KOH. Test for halogen as usual.

e. They are not fully decomposed by potash fusion even.

The polyhaloid cpds. offer less resistance to these reagents.

X. *c*. When the halogen is removed in the dry way as by hot zinc dust, the ring residues generally unite. Similarly with sodium in presence of dry ether, the two rings unite. So also, if the arylhaloid be mixed with aliphatic halide, the residues unite, forming alkylaryl cpd.

See Preparation of Ethylbenzene. Similarly Diphenyl, Ditolyl.

XIII. They show the typical Aromatic reactions.

a. Sulphonation.
b. Nitration.
} These happen in the usual way, the substances dissolving in the strong acids used.

k. They show also the usual condensation reactions with $AlCl_3$.

CHAPTER XII.

NITRO DERIVATIVES:

NITRO GROUP ATTACHED TO RING.

Mono cpds., RNO_2.

These are liquids and solids, with the characteristic nitro smell, of definite b.p. and m.p., more or less yellow in colour. They are insol. in water, sol. in organic solvents.

I. *a*. Very combustible, as containing the oxidising NO group, burning readily with smoky flame.

Try with *nitrobenzene*.

Wet way oxidation is resisted by nitrobenzene, but, as in the hydrocarbons, side-chains are oxidised, often completely, nitroaromatic acids being formed.

b. Test *nitrotoluene* with $KMnO_4$ as toluene.

II. *a*. Dry way reduction with hot zinc dust is rather violent; naturally.

Wet way reduction: the group test.

b. Stannous Chloride and conc. HCl.

Mix the nitro body with the HCl in a little flask (or in a stoppered bottle). Warm, and add the $SnCl_2$ drop by drop, until the nitro smell has nearly or quite gone. Cool and dilute a little. Test one part with H_2S: a yellow pp. of SnS_2 (instead of brown SnS) proves the oxidation of the stannous cpd. Test another part for primary amine (isocyanide test *q.v.*). This completes the proof. Use nitrobenzene.

Other reducing reagents, of gradually increasing power, reduce the nitro-cpd. successively to azoxy, azo, hydrazo bodies, the latter on addition of conc. HCl passing into diarylene diamines. See Benzidine.

V. *a.* They may be halogenated as usual, like the Hydrocarbons.

c. Sodium does not replace hydrogen. Compare Aliphatic Nitro bodies.

IX. They are quite unhydrolysable, being unacted upon by dil. acids or alkalis.

XI., XII. They show neither acid nor basic reactions. Compare aliphatic nitro cpds.

XIII. *a.*, *b.* They may be sulphonated and further nitrated in the usual ways.

g. Being tertiary cpds. they do not react with nitrous acid. See below the Aliphatic Nitro cpds.

*Aliphatic Nitro Bodies.

These differ from the above in the following points:—

V. *c.* Sodium replaces one H atom, that attached to the C atom next the nitro group.

XII. *f.* They show quasi-acid reactions, dissolving in alkalis to form salt-like cpds.—if primary and if secondary: tertiaries, of course, act as above.

XIII. *g.* Salts of the primaries give with nitrous acid a red colour. Secondaries similarly give a blue colour: tertiaries do not react at all.

The mono cpds. are liquids with a sweet ethereal smell.

Like these are the aromatic nitro cpds. in which the NO_2 is in the side-chain, *e.g.* Phenylnitromethane, $C_6H_5CH_2NO_2$.

Poly-Nitro Compounds.

These are solids, nearly colourless, without much nitro smell unless impure, of definite m.p. but apt to decompose (explosively) on distillation. Solubility as for mono cpds.
Use *meta-di-nitrobenzene*: the commonest one.

I. *a.* They are more combustible than the mono cpds. for an obvious reason.

Heat some on a piece of Pt foil.

Wet way oxidation: results similar to those for mono cpds.

II. Dry way reduction as for mono cpds., only more violent.

Wet way reduction: the most important reaction.

b. Stannous chloride, *c.* Tin and HCl: give poly-amino cpds.

Apply the test as described above for mono cpds.

n. Alcoholic ammonium sulphide gives step by step reduction: thus m-dinitrobenzene gives m-nitraniline first. The dinitro cpd. is dissolved in alcohol, ammonia added and H_2S passed in; the liquid is then heated.

In other reactions they resemble the mono-nitro cpds.

CHAPTER XIII.

AMINO COMPOUNDS.

N ON THE RING.

PRIMARY AMINES, MONO, UNSUBSTITUTED.

These are liquids and solids with characteristic odours. They should be colourless, but the liquids have generally a yellow to brown colour (air oxidation). They distil unchanged at atmospheric pressure and have definite m.ps. They are slightly sol. in water (VIII.), sol. in dil. acids (XI.), in organic solvents, not in aq. alkalis (XII.). They are monoacid bases, forming salts with inorganic acids. These are solids often with definite m.p., colourless when made from colourless base, generally sol. and crystalline. Use *Aniline, aniline sulphate, o-toluidine, p-toluidine.*

I. *a.* They are not very combustible, burning with a smoky flame. Their salts behave on heating mainly as NH_4 salts do.

Wet way oxidation: they are very easily oxidised, giving often various complex dyestuffs.

b. Acid dichromate gives at first blue or green dyestuffs, but on warming, quinones are produced (except p-toluidine which gives complex red substances).

Mix the amine with dil. H_2SO_4 and a little $K_2Cr_2O_7$; warm gently. Note the yellow colour and pungent smell of the quinone.

d. Fehling's Soln. does not oxidise them.

f. Ferric chloride behaves like dichromate, giving in the end quinones.

Try with aniline.

h. All are oxidised slowly by atmospheric oxygen, becoming yellow or brown.

k. Dil. soln. of bleaching powder gives with aniline and with o-toluidine a purple colour; p-toluidine gives no colour.

Confirm this.

II. Dry way reduction may give NH_3 and hydrocarbon.

Wet way reduction generally results in hydrogenation of the ring, and seldom in anything else.

V. *a*. Halogenation succeeds very easily, *e.g*. aniline and bromine water give tribromaniline—the mono derivatives are prepared otherwise. The mono cpds. are much weaker bases than the parent base, the trihalogen derivatives are hardly bases at all.

b. When halogenation and oxidation happen together, the product is a haloid quinone; aniline gives chloranil. This is formed using aqua regia.

Try with aniline; note the pungent smell of the chloranil.

c. Sodium with some difficulty replaces one H of the NH_2 group.

VII. 2. *a*. Alkylation: by boiling them with alkyl halides, forming HI salts of secondary, tertiary and quaternary bases. The HI is removed by alkali.

See Preparation of Ethylaniline.

b. The above Na cpd. heated with phenyl iodide gives diphenylamine.

4. Acylation. They form monacyl derivatives easily, and diacyl ones with some difficulty.

See Preparation of Acetanilide.

Warm aniline with acetic anhydride for a few minutes in a t.t. Pour into water; the acyl cpd. is ppd. Filter off, wash and recrystallise from dil. alcohol. Thus acetanilide.

VIII. Their aq. solns. react alkaline to methyl orange, and sometimes even to litmus. The solns. must therefore contain the ions of the real bases, *e.g.* phenylammonium hydroxide, $PhNH_3OH$, from aniline.

Test aq. solns. with methyl orange and with litmus.

IX. They cannot be hydrolysed; but their salts are, in aq. soln., into basic substance and free acid; this can then be titrated in a suitable manner.

Weigh out accurately about 3 gm. of aniline sulphate. Make up to 250 c.c. in a measuring flask. Titrate parts of 25 c.c. with N/10 soda, using phenolphthalein. Estimate thus the purity of the cpd.

The acyl but not the alkyl or aryl derivatives can be hydrolysed by alkalis; others by conc. HI.

XI. *a.* They combine directly with the strong mineral acids, forming solid salts.

Add 10 gm. of aniline to 40 c.c. of dil. H_2SO_4. The pp. is aniline sulphate. Warm up until it dissolves; let it cool. Filter off the crystals at the pump and dry them in air. Use these in IX. above.

Weigh out 2 gm. of aniline from a Sprengel tube into a measuring flask. Make up to 250 c.c. Titrate with N/10 H_2SO_4, using methyl orange.

b. They are displaced by the strong mineral bases.

Take a part of the sulphate prepared above. Shake up gently with caustic soda: globules of aniline are set free. Extract with ether, dry with granules of KOH. Distil off the ether. Thus the aniline.

c. They can displace weak inorganic bases.

Add a soln. of aniline to a soln. of potash alum., $Al(OH)_3$ is ppd.

Aniline heated with NH_4 salts expels NH_3, because though not a stronger base, it is less volatile than NH_3.

XII. *g.* Sodium on heating replaces one H atom of the NH_2 group. A second is replaced only with extreme difficulty. See V. *c*.

XIII. *a*. Sulphonation by conc. H_2SO_4 succeeds easily. The acid is at first added on, forming a salt. On heating it passes to the para position, giving para-amino-sulphonic acids. Paratoluidine gives mainly cpds. in which the CH_3, NH_2, SO_3H groups are in the 1, 4, 3 and 1, 4, 2 positions.

See Preparation of Sulphanilic Acid.

b. Nitration at ordinary temperatures results in the production of much tarry matter, owing to the destruction of the molecule by oxidation, but acyl-anilines, etc., can be nitrated without so much loss. See these.

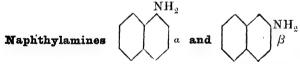
c. With nitrous acid, salts of primary amines condense, eliminating water and forming diazonium salts N⋮N(R)X, at low temperatures.

See Preparation of Benzene Diazonium Chloride.

Dissolve some aniline in excess of dil. HCl and add, drop by drop, cooling well, a soln. of sodium nitrite; the result will be the formation of a yellowish soln. of benzene diazonium chloride, with some evolution of nitroxides. Add then a soln. of β-naphthol in NaOH; the result is the formation of a red pp. of dyestuff.

h. Primary amines react with chloroform in presence of alkalis forming isocyanides, recognised by their intolerable smell.

To a few drops of aniline add some alcoholic KOH, then $CHCl_3$—a few drops—warming. Note the smell of the product.

Naphthylamines

These are solids, generally more or less coloured, of definite m.p. and b.p. They are not very sol. in water, sol. in organic solvents.

They are mono-acid bases, forming salts, most of which are soluble.

In general they react exactly as aniline does.

The α-cpd. has an unpleasant odour. It gives α-naphthoquinone with CrO_3, this having the usual pungent (para-) quinone odour. The α-amine shows a red colour with ferric chloride.

The β-cpd. has no odour and is not coloured by ferric chloride, nor does it give a quinone.

Both can be sulphonated, the products being bodies of some importance in the making of dyestuffs; the 1, 4 derivative is called "Napthionic Acid."

Prove that the α-compound gives a quinone ($K_2Cr_2O_7$ and acid) as under aniline.

Make isocyanides from α and β compounds.

SUBSTITUTED AMINES: IN THE RING, *e.g.* $NH_2C_6H_4X$.

***1. Halogen Arylamines.**

These are generally solids of definite m.p. and b.p., under reduced pressure sometimes; sol. in organic solvents, insol. in water, more sol. in dil. acids, insol. in alkalis. As has been said, the tri-derivatives are commonest, being made directly.

These may in some cases react like the unsubstituted bodies, but they are very much less basic than the parent bodies. The less halogenated ones may form salts, but these are completely hydrolysed by water, *i.e.* the bases may dissolve in conc. acids but on dilution the base is very largely set free. They are also set free by NH_3Aq.

2. **Nitro-Arylamines,** *e.g.* $NO_2C_6H_4NH_2$.

Meta-Nitraniline is the commonest one.

These are solids, generally more or less yellow, but without the nitro smell. They have definite m.ps. but do not distil unchanged. They are insol. in water and in alkalis, sol. in acids and in organic solvents.

I. *a.* They are naturally more combustible than the amines themselves.

Wet way oxidation gives nitro derivatives of the corresponding amino oxidation products.

II. Wet way reduction gives polyamino products if in acid soln., *e.g.* m-nitraniline gives m-phenylene diamine.

They are much weaker bases than the parent amines, dissolving in acids but being reprecipitated by weak bases like ammonia.

Prove that m-nitraniline is a nitro cpd. ($SnCl_2$ and conc. HCl.) See next Section.

Prove that m-nitraniline is a primary amine.

Primary Di-Amines.

-o, m-, p-, **Phenylenediamines,** $C_6H_4(NH_2)_2$.

These are colourless solids, volatilising without decomposition, and with definite m.ps. They become coloured in the air, similarly to other amines.

Their salts, *e.g.* B . 2HCl, are solids, generally sol. and more or less coloured, for similar reasons. The bases are stronger than the monamines.

They react in general similarly to the monamines.

The p-cpd. on oxidation gives quinone.

The m-cpd. (the commonest) with nitrous acid gives a brown pp. or colour, due to the formation of "Bismarck Brown." Hence it is used as a test for nitrites.

The o-, m-, p- compounds give intense red colours with ferric chloride.

They give the isocyanide reaction.

Use m-$C_6H_4(NH_3Cl)_2$ to confirm above, so far as applicable.

***Benzidine is di-Phenylene-diamine,** $(C_6H_4)_2(NH_2)_2$.

This is a colourless solid of definite m.p., insol. in water. It is a di-acid base forming salts like B . 2HCl, etc. The sulphate is rather insol., so may be ppd. and so used as a test. The other reactions are in general similar to those of the monamines; thus it gives a tetrazo cpd. with nitrous acid, and this gives the usual dyestuff with β-naphthol in NaOH.

Secondary Amines, RNHR′.

Alkyl-arylamines are generally liquids of peculiar smell and of definite b.p. They are more or less coloured, for the same reason as the primaries. They are slightly sol. in water, easily

sol. in acids and in organic solvents, insol. in aq. alkalis. Their salts do not crystallise from water and are often sol. in ether. They are monoacid bases of course.

Use *mono-Methylaniline* as type.

I. *a*. Their combustibility is slightly greater than that of the primaries, as the influence of the N atom is less.

Wet way oxidation; results in general not particularly characteristic.

II. *a*. Hot zinc dust may reduce to the hydrocarbon and NH_3.

Results of wet way reduction are not particularly characteristic.

VII. 2. *a*. They may be further alkylated by boiling with alkyl iodide, passing thus into tertiary hydriodide and quaternary iodide. On this is founded a method for their identification as secondary bases.

4. *a*. They can be acylated by acid chloride or anhydride.

Boil a few drops of methylaniline for some time with excess of acetic anhydride in a t.t. Pour into soln. of Na_2CO_3. The acyl compound is ppd. Filter off and recrystallise from dil. alcohol.

VIII. Their aq. solns. are feebly alkaline and :—

IX. *a*. Their salts are largely hydrolysed by water, hence react acid.

d. On boiling with fuming HI, alkyl iodide is set free and primary base produced. This is Zeisel's method of distinction.

XI. *a*. They dissolve in acids, forming salts, but nothing crystallises out, and on adding alkalis, the bases are liberated.

Mix methylaniline with conc. HCl, shaking; add NaOH; note result.

XII. *g.* The imino-H is replaced by Na, but not very easily.

XIII. *a.* Like the primaries, they can be sulphonated and
b. nitrated, and with similar results, *e.g.* the production of much tar in the second case.

d. They condense with nitrous acid, forming yellow oily nitrosamines which give Liebermann's Reaction.

Dissolve methylaniline in dil. HCl, add, drop by drop, a soln. of sodium nitrite until a drop taken out shows excess of nitrite with starch-KI paper. Extract with ether. Separate. Shake up the soln. with NaOH. Separate.

Apply Liebermann's Reaction as follows. Dissolve some colourless phenol in nitrogen-free conc. H_2SO_4 and add a drop of the nitrosamine soln. This should give a deep red coloration, passing into green on dilution and into blue on making alkaline.

Diphenylamine Ph_2NH.

This is a sweet smelling solid, of definite m.p. and b.p., insol. in water and in aq. alkalis, sol. in conc. acids and in organic solvents.

I. It is more inflammable than aniline.

II. With hot zinc dust it may give benzene and ammonia.

VIII. It is not alkaline in reaction and its salts are com-
XI. pletely hydrolysed by water. The base dissolves in conc. acids, but on dilution it is reprecipitated, the acid dissolving in the water.

XII. The imino-H is fairly easily replaced by Na on heating.

XIII. With conc. H_2SO_4 containing even traces of nitroxides, it gives a deep blue colour.

It forms a nitrosamine which gives the Liebermann Reaction.

Confirm I., VIII., XI., XIII.

In reactions VII. 2, 4, it behaves like other secondary amines.

TERTIARY AMINES R′NRR.

Di-alkyl-arylamines are liquids, quite similar in general appearance to the primary and secondary bases. As a group they have a characteristic smell. Solubility similar to that of the secondaries, and their salts resemble those of the secondaries.

Use *Dimethylaniline* as type. Confirm above description.

I. *a*. Combustibility, } similar to those for secondaries.
II. *a*. Complete reduction, }

Try combustibility as usual.

I. Wet way oxidation, } products are uncharacteristic, } samples become coloured by air oxidation.
II. Wet way reduction, }

Bleaching powder does not colour dimethylaniline. Confirm this.

VII. 1. They pass in one stage into quaternary iodides with alkyl iodide.

2. Having no replaceable hydrogen, they cannot be acylated. Hence determine the proportion of dimethylaniline in a sample of methylaniline, thus :—

Weigh out in a Sprengel tube 2 gm. of the sample into a tightly stoppered bottle or measuring flask. Add 5 gm. of acetic anhydride of known strength (do a blank expt.) and heat in a water bath for half an hour. Cool and make up to 250 c.c. Titrate parts of 25 c.c. with N/10 NaOH, using phenolphthalein. Calculate the percentage from the results.

VIII. These amines form stronger bases than the corresponding secondary and primary amines, but their aqueous solns. are hardly alkaline.

IX. *a*. Their salts are largely hydrolysed by water and therefore react acid.

b. Hot conc. HI eliminates alkyl groups as iodides, as applied in Zeisel's quantitative method.

XII. *g*. For the reason given above, VII. 2, sodium has no action.

XIII. *a*, *b*. Sulphonation and nitration proceed as usual, the latter being more successful than with primaries or secondaries.

e. With nitrous acid they give para-nitroso bodies. These on boiling with alkali evolve dialkylamine, leaving paranitrosophenate.

Dissolve some dimethylaniline in excess of dil. HCl, in a t.t. Add sodium nitrite, cooling. Note the reddish brown colour of the HCl salt. Add excess of NaOH; a green pp. of paranitroso body (the free base) is formed.

***Triphenylamine,** Ph_3N.

This is a colourless solid of definite m.p. and b.p., sol. in organic solvents, insol. in water, in alkalis, and in dil. or conc. acids. It forms no salts, *i.e.* is not a base.

*Aliphatic Amines.

These differ from the above in the following points:—

They are much more volatile, most of them are liquids, some even gases, *e.g.* NH_2CH_3. The lower primaries smell like NH_3. Most of them are easily sol. in water.

I. *a*. They are easily combustible, this distinguishing them from NH_3.

Their wet way oxidation products are generally those of the corresponding alcohols, suggesting passage into them first.

VII. 2. Quaternary salts are formed more easily. The hydroxides corresponding to these are obtained as deliquescent solids, very like the alkalis, and like them, strong bases.

VIII. Their aq. solns. are generally strongly alkaline to indicators. Thus they are strong bases, stronger than ammonia in some cases.

XI. *a.* They react easily with dil. acids, forming definite salts crystallisable from water, many of which are neutral to indicators, therefore not appreciably hydrolysed in soln.—only ionised.

c. Their aq. solns. can pp. weak inorganic bases as hydroxides, more easily even than NH_4OH does.

XIII. *c.* Primaries react with nitrous acid, giving at once an evolution of nitrogen, with formation of the corresponding alcohol.

d. Secondaries react as aromatic group, forming nitrosamines.

e. Tertiaries do not react at all.

a. b. They cannot be directly sulphonated or nitrated.

Otherwise they behave quite similarly to the aromatic amines. In particular :—

XIII. *h.* The primaries give isocyanides quite similar to the aromatic cpds.

Those amines containing aryl groups, with the NH_2 group in the side chain, react almost exactly like the aliphatic amines, *e.g.* *benzylamine*, $PhCH_2NH_2$.

ACYL AMINES (mono-acyl, *e.g.* C_6H_5NHCOR).

These are colourless solids with no smell, of definite m.p. generally distilling unchanged under atmospheric pressure. They are not very sol. in cold water, more sol. in boiling water, sol. in organic solvents.

Use *Acetanilide* as a type for the group. Confirm above properties.

I. *a.* Combustibility varies, to a certain extent depending on the acid.

Try as usual with acetanilide and with thiocarbanilide.

Wet way oxidation gives results generally similar to those for the amines themselves, hydrolysis obviously preceding it.

II. Similarly for reduction.

V. They can be directly halogenated, the halogen finally replacing H of the ring.

VII. 2. 4. Alkylation and acylation are possible, one stage only.

VIII. Their aq. solns. are neutral to indicators, showing no ionisation.

IX. *a*. Hydrolysis by even boiling water is a very slow process.

b. Hot dil. alkalis give amine and alkali salt.

Boil some acetanilide with aq. NaOH; the smell of aniline soon becomes apparent. Confirm by adding $CHCl_3$ and boiling again—isocyanide smell.

c. Hot dil. acids give amine salt and the free acid.

Repeat above with dil. sulphuric; note smell of acetic acid in this case.

XI. *a*. They act as very weak bases, their salts being decomposed by water.

XII. *g*. In the cases of the primaries, the remaining H of the NH group can be replaced by Na. The cpd. formed gives pps. with Ag salts, Ag replacing Na.

XIII. *a*. Sulphonation gives, by hydrolysis, the same products as the amines.

b. At fairly low temperatures, nitration goes on without the formation of much tarry matter. Thus at 0° acetanilide gives a mixture of o- and p- nitracetanilides, separated by their different solubilities in chloroform; each gives the amine nitro-derivative on hydrolysis.

d. Those which are NH derivatives behave with nitrous acid as secondary amines do (*q.v.*).

Thiocarbanilide $SC(NHPh)_2$ (from CS_2 and aniline) is the anilide of thiocarbonic acid CS_3H_2. It is a crystalline solid often reacting normally.

CHAPTER XIV.

AZO-, DIAZO-, HYDRAZO-, DERIVATIVES.

These contain two N atoms, respectively doubly, triply (or doubly), singly, linked together. Their stability varies greatly.

***Azo-bodies**, *e.g.* **Azo-benzene**, PhN : NPh.

This is a red crystalline solid, of definite m.p. and b.p., nearly insol. in water and aq. solns., sol. in organic solvents.

I. *a.* On heating in air it burns without explosion with a smoky flame.

II. Alkaline reduction gives hydrazo-benzene (*q.v.*) or aniline. With stannous chloride and HCl it gives benzidine (*q.v.*).

V. *c.* Sodium has no action.

VIII, XI, XII. Soln. neutral to indicators, *i.e.* neither acid nor basic, therefore not ionised in soln.

V *a.*, XIII, *a*, *b*. It can be halogenated, sulphonated, nitrated as usual.

***Diazo-bodies, diazonium salts.**

These appear to exist in at least two forms, true diazo bodies RN : NX where X may be OH. These are unstable substances, acting as pseudo-acids, *e.g.* forming PhN : NOK. But if X be halogen or other acidic radical, the compounds behave as N-substituted ammonium (diazonium) salts, N $\vdots$ N(R)X, and these are slightly more stable. They are colourless solids, mostly sol. in water, less sol. in ether and in alcohol.

I. *a.* The dry salts are very explosive, especially on heating.

Wet way oxidation in alkaline soln. gives nitrosobenzene, PhNO, and phenylnitramine $PhNHNO_2$ (or PhN : NOOH, benzene diazoic acid, as forming, *e.g.* PhN : NOOK).

II. Wet way reduction gives arylhydrazines.
See the Preparation of these compounds.

VIII. The salts are well ionised in soln.; one reason for ascribing the diazonium formula to them.

IX, X. They undergo many interesting and useful transformations :—

Boiled with water, they give nitrogen and phenols. Sulphates are best.

Boiled with alcohol they give N_2, hydrocarbon and aldehyde. Sulphates best.

Halogen salts tend to give N_2 and aryl haloid, when boiled with water. Thus any salt boiled with KI gives aryl iodide.

With Cu_2Cl_2 soln. an addition cpd. is formed and ppd. On boiling, aryl chloride is formed, N_2 evolved. Aryl haloid results on boiling a salt with copper powder and halogen acid.

Similarly on boiling with $Cu_2(CN)_2$ in KCN, nitriles result, *e.g.* PhCN.

XI. *a.* The hydroxide reacts with dil. acids forming the diazonium salts. Some of these are quite like NH_4 salts, *e.g.* the chloroplatinate.

b. Addition of strong bases results in formation of the hydroxide, which generally decomposes more or less, *e.g.* into phenols. See XII.

XII. *a.* With excess of strong alkali, salts such as PhN : NOK are formed.

XIII. They undergo interesting condensations:—

α. With primary amines, forming diazoamino bodies, *e.g.* aniline gives PhN : NNHPh. Here the diazonium salt passes first into a true diazo cpd. These cpds., when mixed with aromatic amine salt (best HCl), pass into aminoazo bodies, *e.g.* in the case quoted PhN : $N.C_6H_4NH_2$, the real product being the salt of this, from which the base itself is obtained by adding alkali, *e.g.* ammonia.

When Reaction XIII *c.* is applied to a primary base, insufficient HCl being present, the diazo-amino body is formed at once as a yellow pp. This may be crystallised from benzene or alcohol as golden yellow plates.

Or, to the powder, more aniline and some aniline hydrochloride are added and the mixture warmed; a deep red soln. results on standing. On adding more HCl small violet needles of the salt are formed; these are washed with dil. HCl to remove $PhNH_3Cl$.

Carry out this as directed above.

Aminoazo-benzene itself crystallises from spirit in orange prisms. It is a primary base like aniline, with similar reactions.

β. With phenolic bodies in alkaline soln.

Make some soln. of diazochloride from aniline (see this). Add soln. of β-naphthol in NaOH. A scarlet pp. of a dyestuff is formed.

This is the confirmation reaction for primary aromatic amines.

***Hydrazo bodies,** *e.g.* PhNH.NHPh, **Hydrazobenzene.**

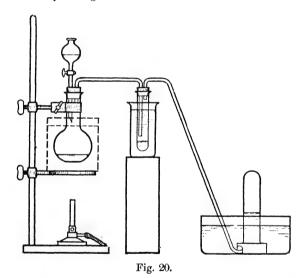
These are colourless bodies with definite m.p., insol. water, sol. in alcohol or in ether. They decompose into azo-body and amine at temperatures above their m.ps. They are indifferent to dil. acids and alkalis, but:—

Conc. acids convert them into benzidine or its homologues (*q.v.*).

HYDRAZINES.

e.g. **Phenyl Hydrazine,** $PhNH.NH_2$, and its salts.

The base is a colourless or faintly yellow liquid, crystallising in large prisms at ordinary temperatures, boiling with some decomposition under ordinary pressures. It is sol. with difficulty in water, easily in organic solvents.

Fig. 20.

It is mono-acid, the salts being colourless crystalline solids, mostly fairly sol. in water. These and the base have generally a yellow to red colour due to air oxidation.

Note those points on a sample of the base and of the hydrochloride.

I. *a*. Not very combustible, burning with a smoky flame.

Try with the base as usual.

Wet way oxidation succeeds in many ways :—

d. Fehling's Soln. gives benzene and nitrogen.

Fit a small flask with a dropping funnel and delivery tube leading to the bottom of a t.t. with cork and delivery tube, and standing in a beaker of ice water. Some form of absorption tube may be used instead. From this proceeds an ordinary gas-delivery tube for collection over water. Put into the flask 75 c.c. of Fehling's Soln. with 25 c.c. of NaOH. Drop in through the funnel a soln. of the hydrochloride in water while the Fehling's Soln. is kept boiling, until this is nearly all reduced. Water and benzene condense in the t.t. to be separated and the benzene identified as usual, while the nitrogen passes on to be collected over water (Fig. 20).

A quantitative method based on this, wherein the N_2 is measured, serves to determine the presence and amount of CO groups in a cpd., this being made to form a hydrazone, or osazone, not oxidised by Fehling's Soln.

f. Ferric chloride also gives the corresponding hydrocarbon and nitrogen.

Fit a t.t. with a delivery tube dipping into a little water in another t.t. standing in a beaker of water. Boil a little of the base with the $FeCl_3$. Collect and identify the C_6H_6.

Mercuric oxide gives diazo cpd. with the sulphate in the cold.

II. *a.* Dry way reduction gives at first aniline and NH_3, and these are the final products of wet way reduction.

V. *a.* Halogens give replacement in the ring, finally.

The para-Brom- cpd. is used as a substitute for the parent body.

c. Sodium, on heating, replaces H, forming red amorphous $PhNNa.NH_2$.

VII. 2. *a.* Alkyl iodides give the HI salts of alkylated hydrazines, either or both N-groups acting.

4. *a.* Acyl hydrazines are obtained in the usual way, the acyl groups going first to the NH_2 group.

VIII. The soln. of the base is only slightly alkaline.
Try an aq. soln. with methyl orange.

IX. *a*. The Na derivative is completely, and the salts are largely hydrolysed by water.

b. The acyl derivatives are hydrolysed easily by hot dil. alkalis or acids.

d. The alkyl derivatives only by hot conc. HI, as usual.

XI. *a*. The base and its alkyl derivatives form true salts, the acid attaching itself to the NH_2 group. The acid in these can be titrated. See aniline.

To a quantity of conc. HCl add an equal volume of water, then gradually drop in the base. The HCl salt comes out as a pp. of crystalline flakes. Filter at the pump. Wash with HCl dil. Press well and dry.

Heated in an open dish this salt sublimes without melting.

b. Dil. alkali sets free the basic part from these salts, extracted by ether.

XIII. *a*, *b*. Sulphonation and nitration: as in the case of aniline.

d. With nitrous acid it behaves as a secondary amine, *i.e.* the NH group reacts, but in certain cases phenyl azoimide $C_6H_5N_3$ is the result.

XIV. 2. *b*. The base and its unsymmetrical alkyl derivatives form hydrazones with simple aldehydes and ketones (*q.v.*), osazones with hydroxy-aldehydes and ketones, *i.e.* the sugars (*q.v.*).

CHAPTER XV.

SULPHONIC DERIVATIVES.

Obtained by Reaction XIII. *a.* applied to the hydrocarbons and their derivatives, SO_3H on the ring.

SIMPLE SULPHONIC ACIDS

(*i.e.* of the *hydrocarbons*) and their salts.

The acids are very deliquescent crystalline solids, very sol. in water, less sol. in those organic solvents on which they cannot act.

They decompose on heating into various products.

Their salts are crystalline solids, nearly all sol. in water easily, but not in NaCl soln. See VIII.

Use *Potassium Phenylsulphonate*, $C_6H_5SO_3K$.

I. *a.* Combustible in part, leaving C residue containing acid sulphate.

Try this. Test residue with litmus after adding a drop of water, reaction acid.

Wet way oxidation as for the original hydrocarbon, generally.

II. *a.* Heating with hot zinc dust gives peculiar-smelling products, including thiophenol, PhSH, etc., and some ZnS.

Try this as usual. Note the smell, and also after adding a drop of acid.

Wet way reduction gives sulphinates, and then thiophenates.

V. *a.* Halogens cause substitution in the ring as usual.

c. Sodium, of course, acts on the acids as usual.

VI. Phosphorus chlorides give sulphonic chloride, *e.g.* $PhSO_2Cl$.

See the Preparation of Benzenesulphonic Chloride.

† Dry a little $PhSO_3K$ carefully, mix carefully in a t.t. with PCl_5 and heat gently. Note the peculiar smell of the sulphonic chloride.

VII. 2. *a.* The acids form estérs with alcohols in the usual manner.

b. The salts do so when heated with alkyl iodides.

When the salts are heated with KCN or dry K_4FeCy_6, nitriles result.

Mix thoroughly well-dried $PhSO_3K$ with KCN. Heat in a t.t. Note the smell (like nitrobenzene) of the PhCN produced.

VIII. The acids can be exactly titrated, *i.e.* are strong acids. The salts are well ionised, but less so than some inorganic salts.

Heat a quantity of benzene with conc. H_2SO_4 until sulphonation is nearly complete. Add NaCl in excess. A crystalline pp. of $PhSO_3Na$ results.

IX. *e.* Neither the acid nor its salts are easily hydrolysed, except by potash fusion—the group test.

See Preparation of Phenol.

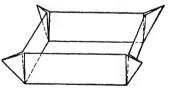



Fig. 21.

Pinch up the corners of a piece of copper foil so as to make a boat or tray about 5×3×1 cm. (Fig. 21). Fuse a little caustic potash in it. When in quiet fusion, dust in the sulphonate, $PhSO_3K$ here. Heat until it begins to turn brown, then let cool. Put into a beaker of water. Acidify with dil. H_2SO_4. Note effervescence of SO_2 (smell) and presence of hydroxy body, phenol here, by smell and by ether extraction. Evaporate

off the ether and identify the OH cpd. by the appropriate tests. See these, Chap. XVI.

Heating with soda-lime gives a similar result, but the OH cpd. (phenoloid) may remain combined, largely.

X. By heating in a current of superheated steam, H_2SO_4 is eliminated, and the original hydrocarbon regenerated.

By heating alone, sulphones may be produced, and a sulphate left.

Heat a small quantity of well-dried K salt in an ignition tube. Note the peculiar smell produced, and prove that a sulphate is left.

XII. The acids neutralise alkalis, decompose carbonates, etc. They are obtained free by adding dil. H_2SO_4 to the Ba salt or by the action of H_2S on the Pb salt; these salts are produced by neutralising the original mixture with the carbonates.

XIII. *a.* Further sulphonation requires the use of fuming sulphuric acid.

b. Nitration is carried out in the usual fashion.

1. ***Sulphonic Chlorides,** *e.g.* $PhSO_2Cl$.

These are colourless liquids of unpleasant smell, insol. in water (see below), sol. in those organic solvents on which they cannot act, boiling nearly unchanged.

The reactions correspond almost exactly to those of carboxylic acid chlorides, *e.g.* acetyl or benzoyl chlorides: except that:—

II. On wet way reduction they give first sulphinic acids then mercaptans; and:—

IX. *a.* They are not acted on by water, except on long standing or on boiling, when the normal reaction happens.

b. The action of alkalis is slower than in the case of carboxylic chlorides.

2. ***Sulphonamides,** *e.g.* $PhSO_2NH_2$.

These are well-crystallised solids of definite m.p., hence frequently used for identification of particular sulphonic acids. They are insol. in water but sol. in organic solvents.

Their reactions are similar to those of the carboxy-amides like acetamide or benzamide; except that they are, as a rule, slower in reaction than these; and:—

IX. *e.* They are not easily hydrolysed by any reaction milder than potash fusion.

3. ***Sulphonyl Esters,** *e.g.* $PhSO_2OEt$.

These are mostly liquids, distilling only in a vacuum, corresponding more or less to carboxylic esters.

Boiled with alcohols they give ethers and sulphonic acid, a method proposed for preparing the former instead of the usual method with alkylsulphates. They give sulphonate and alcohol on alkali hydrolysis.

4. ***Poly-sulphonic Derivatives.**

These and their salts react in general quite normally, sometimes in definite stages, but the three disulphonic acids on potash fusion may give only one dihydroxy benzene, viz. the meta, resorcinol (*q.v.*) at a very high temperature.

5. ***Sulphonic Derivatives of Substituted Hydrocarbons:**

e.g. Chlor- Nitro- benzenesulphonic acids and their salts react quite normally, giving, *e.g.* on hydrolysis by potash fusion, chlor-nitro-phenols, but in the former case the other substituent may be replaced as well and dihydroxy benzenes are formed, especially the meta-, resorcinol.

6. **Amine Sulphonic Acids.**

Of these the most important is *Sulphanilic Acid*, $H_2NC_6H_4SO_3H$, the para cpd.

This forms platy crystals, $+H_2O$, efflorescing in air, slightly sol. in water and in alcohol. Its salts are sol. in water, insol. in NaCl soln.

Use the acid.

I. *a*. Not easily combustible, burning with a smoky flame.

b. Wet way oxidation as by acid dichromate gives benzoquinone (*q.v.*).

Warm together in a t.t. Note smell of the quinone.

V. *a*. With bromine water it gives a pp. of tribromaniline easily.

Try this.

VIII. It is a fairly well ionised acid and its salts are also well ionised.

Try its reaction with litmus.

IX. *e*. Potash fusion is required for hydrolysis, but it then gives aniline and a sulphate, not aminophenol and a sulphite, the normal result expected.

Show that the residue from this contains a sulphate, not a sulphite.

The aniline is volatilised so that it can hardly be identified.

XII. *a*. The acid neutralises hydroxides and decomposes carbonates.

b. The acid is ppd. from conc. solns. of its salts on adding dil. H_2SO_4.

c. None of its salts is really insol.

XIII. *c*. Being still a primary amine, it gives the Diazo Reaction.

Test as usual with dil. sulphuric and sodium nitrite, adding β-naphthol in NaOH to the product.

h. It should give the Isocyanide reaction.

Try as usual.

CHAPTER XVI.

HYDROXY COMPOUNDS.

These are again of two classes (α) those having the OH attached to the ring, hydroxy-benzenes, etc., now to be described. (β) Those having the OH in the side chain to be described in Chapter XVII. Aromatic Alcohols.

MONO-HYDROXY-BENZENES, -NAPHTHALENES, ETC.

PHENOL C_6H_5OH : CRESOLS $CH_3C_6H_4OH$.

Phenol is a solid, o- and p-cresol also solids, m-cresol a liquid. Commercial cresol or "cresylic acid," a mixture, is a liquid. Those that are pure cpds. have a definite m.p. and b.p.

They are sol. in water, in acids, in alkalis, and in organic solvents.

Use *phenol* crystals, *cresylic acid*, *p-cresol*.

I. *a*. They are combustible, but of course less so than the hydrocarbons.

Try phenol and "cresylic acid."

Like the hydrocarbons, they are not easily oxidised, the products often being uncharacteristic. Any side chains as a rule resist oxidation; thus o-cresol does not give salicylic acid.

II. *a*. Dry way reduction. Hot zinc dust gives the corresponding hydrocarbon.

Heat a little phenol in a hard glass tube with excess of zinc dust. Collect the benzene as usual and identify it. (See Fig. 1.)

Wet way reduction as for the hydrocarbons.

V. *a*. Halogens easily give substitution, generally as far as the tri-derivative, as with phenol and the cresols.

Dissolve a little phenol in water. Add bromine water in excess. Tri-bromphenol is ppd., nearly white. It may be crystallised as usual from alcohol.

c. Sodium as usual replaces H of the OH group present, forming quasi-salts.

VI. Phosphorus pentachloride should similarly replace the OH group by halogen, but the action is not complete, and part reacts in a different way.

VII. 2. *b*. Phenol ethers, anisol, phenetol, are produced by the interaction of phenate and halogen cpd. and similarly for cresol ethers.

3. *a*. Phenol, etc., with conc. H_2SO_4 gives phenyl, etc., sulphuric acids, *e.g.* $PhO.SO_2.OH$, etc., which readily pass into phenol, etc., sulphonic acids. See XIII. *a*.

4. *b*. Acylation is generally carried out by the Schotten-Baumann method.

Mix 4 gm. of phenol with 2 gm. of NaOH in water in a t.t. well corked. Add 6 gm. of PhCOCl and shake well until the smell has gone. Separate the oil, cool well, and rub with a rod until solid. Filter off, wash with water, and dry. Recrystallise from alcohol.

VIII. Their aq. solns. react acid to litmus and phenolphthalein but not to methyl-orange, that is, ionisation to a limited extent has happened.

Try this in the ordinary manner.

XII. *a*. They react with alkalis and with certain metallic oxides, but do not dissolve carbonates. See Metallic Salts.

Try phenol and "cresylic acid" with NaOH, and phenol with milk of lime.

b. They are removed from these salts by almost any acid (see sodium phenate).

d. In absence of acids, they all give coloured products with ferric chloride, phenol violet, cresols blue.

Try with phenol and with "cresylic acid."

XIII. *a.* Sulphonation proceeds easily on warming with conc. sulphuric. See VII. 3, *a.*

b. Nitration proceeds rather violently, with the production of much tarry matter, containing the o- cpd.—volatile with steam, and the p- cpd. left with the tar, and crystallising out from that on washing with hot water. The tri-nitro cpd., picric acid, is obtained by sulphonating first and then nitrating with fuming acid.

See the Preparations of o- and p-Nitrophenols, Picric Acid.

f. Reaction with Nitrous Acid: Liebermann's Reaction.

Dissolve the phenolic body in conc. H_2SO_4. Add more conc. H_2SO_4 in which a trace of $NaNO_2$ has been dissolved. Thus a cherry red colour is obtained. Add water, it becomes green. Make alkaline, it turns to blue.

With dil. acid and nitrite, p-nitrosophenol results, crystallising from hot water in colourless needles, sol. in ether with a green colour.

j. Unlike the aliphatic OH cpds., phenols as a group react with NH_3 in presence of a dehydrating agent, say $ZnCl_2$, *i.e.* on heating with zinc-ammine chloride, forming amines. Thus phenol gives aniline, etc.

NAPHTHOLS, [OH] *α* AND [OH] *β*

These are colourless or slightly pink solids of quite different m.p., but with nearly the same b.p. They differ to a certain extent in smell as well as chemically. They are nearly insol. in cold water, more sol. in hot, sol. in alkalis, and in organic solvents. They react quite similarly to phenol.

Compare the two forms and use both for the following tests.

I. *a.* Combustion, flame more smoky than for phenol.

II. *a.* Hot zinc dust gives naphthalene.

Try this with both forms, as for phenol.

XII. *d.* With ferric chloride, α gives violet flakes; β a green pp. Confirm this.

XIII. *d.* Nitrous acid in the presence of a dehydrating agent gives nitroso-naphthols. Nitroso-β-naphthol is used as a reagent for separating nickel and cobalt, the latter being ppd. even in presence of conc. acids. Fe and Cu also ppd. in presence of HOAc.

Dissolve 20 gm. of β-naphthol and 15 gm. of $ZnCl_2$ in 125 c.c. of boiling alcohol. Add 20 gm. of $NaNO_2$ in 40 gm. water, slowly. On standing overnight the Zn salt crystallises out from red liquid. Filter, wash with alcohol, and warm up with 18 gm. of NaOH in 240 c.c. water. Stir well. Cool and filter at the pump. Wash with water. Decompose with 25 c.c. of dil. HCl. Filter, wash with water, and recrystallise from alcohol.

V. *a*, *c*, VI., VII. 2. *b*, 3. *a*, 4. *b*, VIII., XII. *a*, *b*, XIII. *a*, *b*. In all these reactions the naphthols behave exactly like phenol

Metallic Salts of Phenols, *e.g.* PhONa.

These are solids, generally deliquescent, and smelling of the phenol. As the phenols, etc., are very weak acids, these salts are slowly decomposed by atmospheric carbonic acid; hence the use of the Ca salt as "disinfecting powder." Also in aq. soln. they are very largely hydrolysed; hence the strongly alkaline reaction. Dil. acids hydrolyse them entirely, the phenol set free possibly rising to the surface as an oily layer or in any case extractable by an immiscible solvent, *e.g.* ether. This soln. is dried by Plaster of Paris, the ether distilled off, and the phenol identified by b.p. and by the proper tests.

Take a specimen of Sodium Phenate, note its smell and its alkaline reaction. Dissolve part in water, pass in a current of washed CO_2. Then extract with ether. Separate, etc. Identify the phenol.

To another part add dil. H_2SO_4. Note any layer, extract with ether, etc.

Phenol Ethers, *e.g.* **Anisol,** PhOMe ; **Phenetol,** PhOEt.

These are colourless liquids of definite b.p., of characteristic smell, insol. in water and aq. liquids, sol. in organic solvents. They are very stable; undergoing halogenation, sulphonation, nitration almost like the hydrocarbons; they are not reduced by hot zinc dust.

I. *a.* Naturally, they are more combustible than the phenols.

IX. *d.* Like other ethers, they are hydrolysed only by fuming HI hot, Zeisel's Reaction.

Phenol Esters, *e.g.* **Acetate,** PhOAc ; **Benzoate,** PhOCOPh.

These are colourless liquids and solids, of definite m.p. and b.p., insol. in water and aq. liquids, sol. in organic solvents.

I. *a.* Combustible, burning with smoky flame.

IX. *b.* They are easily hydrolysed by boiling with dil. alkalis, these reacting with both parts. To separate, pass washed CO_2 through the liquid ; the phenate gives free phenol, extracted with ether ; the other salt is not decomposed. See Salol, phenyl salicylate.

SUBSTITUTED PHENOLS.

1. **Haloid Phenols,** *e.g.* **Tri-Chlor., -Brom-Phenol,** 1 OH, 2, 4, 6, Cl or Br.

The tri-chlor. cpd. forms a woolly mass, the tri-brom. long needles, both colourless, with peculiar smell, powerful antiseptic action, definite m.p. They are slightly sol. in water, easily sol. in alkalis, and in organic solvents.

I. *a.* Of course, much less combustible than phenols.

II. *f.* Sodium and alcohol gives the parent phenol.

Prove the presence of halogen in trichlorphenol.

VIII. They react more strongly acid than the original phenol.

Try with litmus and phenolphthalein.

IX. *a.* Their salts are less hydrolysed in aq. soln. than phenates.

e. Potash fusion hydrolyses them completely, removing all the halogen.

The o-, m-, p-, monobromphenols give resorcinol (meta) thus.

2. **Nitrophenols, mono,** $HOC_6H_4NO_2$, *e.g.*

o-Nitrophenol.	*p-Nitrophenol.*
Yellow needles, with characteristic sweetish phenolic smell, fairly sol. in water, volatile in steam.	Colourless or pale yellow fine needles, faint sweetish smell, less sol. in water, not volatile in steam.

Both are easily sol. in alkalis and in organic solvents, they have definite m.ps. and b.ps. The sodium, etc., salts are quite definite sol. cpds.,

dark red plates or needles.	yellow to brown prisms.

I. *a.* Easily combustible, deflagrating on overheating, like most nitro cpds.

Try this with the ortho-cpd. and its Na salt.

They are not oxidised in the wet way.

II. *a.* Dry way reduction, as by hot zinc dust, is rather violent, naturally.

Wet way reduction is quite normal, resulting finally in aminophenols.

Test both in the usual way with $SnCl_2$ and HCl, confirming the oxidation of the $SnCl_2$, and the production of aminophenols as below.

VI. Phosphorus halogenides act normally, giving halo-nitrobenzenes.

VII. 1. *b.*, 4. *b.* They form ethers and esters similarly to phenol, but these cpds. are made more commonly and easily by nitrating the phenol ethers and esters, as also the halo-phenol-ethers and esters by halogenating the same cpds.

VIII. Their aq. solns. show an acid reaction to litmus, stronger than that of the parent phenol. The colour of an aq. soln. of the p-cpd. is much stronger than that of the crystals, and deepens on dilution owing to more complete ionisation. Therefore it is used as an indicator.

IX. *a.* Their alkali salts show an alkaline reaction, being evidently partly hydrolysed in water. These show the colour of the negative ion.

Confirm the statements above, VIII. and IX., for both forms.

XII. *a.* They react with alkalis and even decompose carbonates, to some extent.

b. They are removed from their salts by stronger mineral acids,

ppd. from strong solns. only.	ppd., unless soln. be very dilute.

d. They do not give the ordinary phenol colour reaction with $FeCl_3$.

Confirm these reactions.

XIII. *a*, *b*. They can be sulphonated and nitrated in the usual manner.

They give Picric Acid in the latter case.

Meta-nitrophenol is of much less importance. It of course reacts similarly to the above, but on further nitration it gives an isomer of picric acid.

Picric Acid is Trinitrophenol, 1, OH, 2, 4, 6, NO_2.

This crystallises from hot water in yellow plates, from non-ionising organic solvents, *e.g.* petroleum ether, in colourless needles. It is less sol. in cold water, and in dil. acids, sol. in alkalis. It has a definite m.p.

The salts are yellow, and sol. in water, especially if hot.

I. *a.* The acid deflagrates on heating above its m.p.; so also do its salts, some of which are dangerously explosive.

Try with small quantities of the acid and of potassium picrate.

II. *a.* Dry way reduction, *e.g.* with hot zinc dust, is highly dangerous.

b. Complete wet way reduction gives triaminophenol.

n. Alcoholic ammonium sulphide gives "picramic acid" monaminodinitrophenol.

Prove that picric acid contains nitro groups, by usual method.

VI. PCl_5 gives picryl chloride, 1, Cl, C_6H_2, 2, 4, 6, NO_2, a true acid chloride, regenerating the acid with water.

VII. 3. The acid forms esters in the usual manner, but as in the preceding cases, these are more easily made by nitrating the phenol ethers.

VIII. Its aq. soln. distinctly affects indicators, therefore contains H ions. The negative picric ion is yellow. In the colourless solns. in ether, petroleum ether, etc., there is evidently no ionisation. The salts are:—

IX. Well ionised and are only slightly hydrolysed by water.

X. Barium picrate boiled with baryta water gives Hydrocyanic acid (!).

XII. *a.* The acid reacts with bases and decomposes carbonates easily.

Confirm the acidity of the aq. soln. of acid, and the neutrality of a salt soln. sodium picrate.

Try the effect of the acid on Na_2CO_3.

b. Removal of the acid from the salts by dil. acids, *e.g.* H_2SO_4, succeeds mainly because picric acid is rather insol. in cold water.

c. Its sodium salt has been used as a precipitant for potassium, since the K salt is only slightly sol. in cold water.

d. It gives no reaction with ferric chloride.

XIII. With KCN soln. it gives "potassium isopurpurate," $C_8H_4N_5O_6K$.

Try this: a deep red solution results.

3. **Aminophenols** $HOC_6H_4NH_2$, **o-** and **p-** most important.

Solids, generally coloured brown or red by light and air, of definite m.p. Not very sol. in water, sol. in organic solvents, sol. in alkalis, forming no definite phenolic salts, and in inorganic acids, forming definite solid inorganic salts also coloured as above, and generally easily soluble in water.

I. *a.* They are not very combustible.

b. Acid dichromate converts the p-cpd. into benzoquinone. Confirm this.

h. They are easily oxidised by air, especially in alkaline soln., hence the colour. They act as powerful reducing agents, hence their use in photography as developers.

II. *a.* Hot zinc dust should convert them into benzene and ammonia.

VII. They can form ethers and esters quite normally, but the former are made generally by the reduction of nitrophenol ethers, the latter normally.

Phenacetin, the antipyretic, is acetparaphenetidin or p-acetaminophenetol, $EtOC_6H_4NHAc$, or $C_2H_5O.C_6H_4.NHCOCH_3$.

VIII. Their solns. in water are not alkaline and :—

IX. *a.* Their salts are largely hydrolysed by water, so react acid.

Prove that the p-cpd. HCl salt is acid, HCl can be titrated.

b, c. The esters can be hydrolysed by alkalis and by acids.

Find the aceto group in phenacetin by boiling with dil. H_2SO_4.

d. The ethers are hydrolysed by hot conc. HI only—Zeisel's Reaction.

XI. Their basic function is stronger than their acidic (phenolic) function. See above, general properties, and solubility, also IX.

XII. *d*. They react with ferric chloride, as phenols and as amines.

Add $FeCl_3$ to the bases or to neutralised salt solns. Both give the usual violet colour. Warm, para passes into yellow quinone.

XIII. *c*. Nitrous acid gives diazo cpds. in the usual manner and these react as usual with β-naphthol in NaOH, producing a red colour or pp.

h. They should give the isocyanide reaction as primary amines.

The o-cpd. enters into condensation reactions with very many different kinds of substances, forming heterocyclic bodies, of many kinds.

4. ***Phenolsulphonates,** $HOC_6H_4SO_3H$, **p**- cpd. most important, then **o**.

The acids are colourless solids, deliquescent and easily sol. in water. Their sulphonic salts are colourless solids easily sol. in water. Both acids and salts show a double set of reactions, those of the phenols and those of sulphonates, and their properties are exactly the sum of the reactions for each of these groups. See those for reactions, V *c*., VI, VII.

Use zinc (or potassium) p-phenolsulphonate.

I. *a*. Salts not very combustible, leave a residue of sulphate (or sulphide—ZnS).

b. Acid dichromate oxidises the p-cpd. to benzoquinone.

Confirm these points.

II. *a*. Hot zinc dust gives finally phenyl mercaptan (and zinc sulphide).

IX. *e*. Potash fusion: salts of p-cpd. give diphenols $C_{12}H_8(OH)_2$: o- gives catechol—normally.

Polyhydroxybenzenes.

Di-hydroxy Benzenes, $C_6H_4(OH)_2$.

o-: Catechol.	*m-: Resorcinol.*	*p-: Quinol or Hydroquinone.*
Pearly plates, peculiar smell.	Opaque white needles, sweet taste.	Fine sparkling needles, bitter taste.

They all have definite m.ps., and definite b.ps. except Quinol which decomposes. All dissolve more or less easily in water, in organic solvents, and in alkalis.

I. *a.* All burn fairly well with smoky flame, leaving carbon residue.

d. Fehling's Soln. acts as follows:—

C. is oxidised.	R. not oxidised.	Q. is oxidised.

e. Tollens's Reagent gives the following results:—

Oxidised.	Oxidised.	Oxidised.

h. In aq. soln. all are easily oxidised by air, especially in alkaline soln.

C. becomes green, then brown to black.	R. becomes brown.	Q. becomes green, then brown; quinone formed.

Confirm these statements, *d*, *e*, *h*.

II. *a.* By heating with zinc dust all give benzene (and phenol if incomplete).

VII. They give ethers and esters in the usual way, but in two stages.

VIII. The aq. solns. are hardly acid to indicators; *i.e.* no extensive ionisation occurs.

IX. Of course they cannot be hydrolysed, but their ethers and esters can be, by methods *d.*, and *b.* or *c.* respectively.

XII. *a.* Their solns. in the alkalis do not contain definite salts.

c. With lead acetate they react as follows:—

White pp.	No pp.	Pp. white in presence NH_3.

d. Ferric chloride gives phenolic reactions with *o.*, and *m.*: oxidises *p.*

Green; violet to red with $NaHCO_3$	Dark violet.	Green needles, quinhydrone; then yellow, quinone.

Carry out these reactions with ferric chloride.

XIII. All give condensation reactions with phthalic anhydride, forming—

Alizarin.	Fluorescein.	Quinizarin.

Heat the two together for a time with a little conc. H_2SO_4. Pour the "melt" into water, make alkaline with NaOH. Note colour.

Purple colour.	Green fluorescence.	Purple colour.

Phenol itself in this reaction gives phenolphthalein; red with NaOH.

Guaiacol, the monomethyl ether of catechol, is a yellowish liquid if from wood tar, or a colourless crystalline mass if synthetic, of peculiar persistent smell. It has a definite m.p. and b.p. It is sol. in water to some extent, and easily in alkalis and in organic solvents.

In its reactions it resembles catechol, but is less easily oxidised by air.

IX. *d.* It gives catechol and methyl iodide with hot conc. HI—Zeisel's method.

XII. *a.* Its salts with alkalis are fairly definite but are hydrolysed in soln.

d. It gives an emerald green colour with ferric chloride. Try this.

Catechol and *guaiacol* form salts with some inorganic acids, *e.g.* sulphite and carbonate.

Trihydroxybenzenes, *e.g.* **Pyrogallol** 1, 2, 3.

This is a very fine light white powder or larger needles, of definite m.p. It is very sol. in water, less so in alcohol and in ether.

I. *a.* It is only slightly inflammable.

d. Fehling's Soln.
e. Tollens' Reagent. } Both these are rapidly reduced by it even in the cold, with formation of oxalic and acetic acids.

h. Aq. solns. absorb oxygen very rapidly if alkaline, turning brown and decomposing into CO_2, acetic acid, etc. Hence its use in gas analysis.

Confirm these statements.

VII. 2, 4. It yields ethers and esters in the usual manner, in three stages.

VIII. Though called pyrogallic acid, it has not an acid reaction.

XII. *a.* It dissolves in alkalis but forms no definite salts.

d. Ferric chloride gives with it a red colour.
$Fe_3(SO_4)_4$ *i.e.* partly oxidised $FeSO_4$ gives a blue-black colour.

e. Lead acetate gives a white pp. of $C_6H_3(OH)_3.PbO$.

Try these tests.

Phloroglucinol, sym. trihydroxybenzene 1, 3, 5
Hydroxyhydroquinone 1, 2, 4, } are the other isomers.

They are of little practical importance.

Quinones.

These are aromatic cpds. in which two hydrogen atoms are replaced by two oxygen atoms, in the o- or p- positions. The latter are the more important. They react either as peroxides, see II, VI, or as diketo-derivatives of di-hydroaromatic cpds.

The para-quinones are yellow crystalline solids, generally with peculiar pungent smell, of definite m.p. and b.p. but subliming readily, volatile with steam, slightly sol. in water, easily sol. in organic solvents.

I. *a*. They are fairly easily combustible, burning with the usual smoky flame.

II. *a*. With hot zinc dust, they give the simple hydrocarbon, not the dihydrogenised one.

m. Sulphur dioxide gives the tertiary di(OH) cpd., not a secondary di-(CHOH) cpd. Compare ketones.

They act as oxidising agents, compare ketones. Thus phenylhydrazine is oxidised by them, instead of forming a hydrazone. See XIV. 2.

III. *a*. They add on the number of Br. atoms proper for a dihydrogenised cpd. *e.g.* benzoquinone, two or four; naphthoquinone six, etc.

VI. The action of PCl_5 *e.g.* gives p-dichlor cpds. identical with those from the corresponding di (OH) cpd.

XIV. 1. *d*. They do not always add on sodium bisulphite; phenanthrenequinone does.

2. *a*. They form with H_2NOH, mono- and di-oximes, the mono being considered the same as nitrosophenol. Compare ketones.

Benzoquinone (para) long yellow needles, and α-**naphthoquinone,** also **p,** yellow plates, may be considered as types.

β-**Naphthoquinone,** red needles, is odourless and nonvolatile and decomposes on heating. It is an ortho-quinone.

Anthraquinone, para, yellow needles, shows in general normal reactions but is not reduced by SO_2. It can hardly be described as an oxidising agent.

Phenanthraquinone, ortho, orange-yellow needles, melts and distils without decomposition, is odourless, nonvolatile with steam, not reduced by SO_2.

Benzoquinone

α-Naphthoquinone

β-Naphthoquinone

Anthraquinone

Phenanthraquinone

CHAPTER XVII.

HYDROXY COMPOUNDS AND THEIR DERIVATIVES.

In these the replacement (by OH, etc.) is in the side chain.

AROMATIC ALCOHOLS AND THEIR DERIVATIVES.

e.g. **Benzyl Alcohol,** $C_6H_5CH_2OH$, **primary.**

This is a sweet-smelling, colourless liquid, of high b.p., somewhat sol. in water, dil. acids, and in alkalis, less sol. in salt solns., sol. in organic solvents. In it the primary alcohol properties are more predominant than those of the aromatic nucleus.

I. *a.* Combustible, burning with a smoky flame.

Confirm this as usual.

c. Wet way oxidation gives benzaldehyde and finally benzoic acid, normally.

Warm it with alkaline $KMnO_4$ in a stoppered bottle or in a flask in a water bath. Identify the acid as usual, after removing the pp. by SO_2 or after filtering off.

g. Even conc. HNO_3 oxidises it first, though it may nitrate the products.

II. *a.* Dry way reduction should give toluene.

V. *b.* Halogens are more likely to cause oxidation than replacement.

c. Sodium replaces the OH hydrogen normally, though slowly.

VI. Phosphorus halogenides give benzyl halide—normally.

VII. 1. Etherification, and 3 Esterification: as usual.

4. *b*. Acylation by the Schotten-Baumann method goes quite normally.

X. *a*. The benzylsulphuric acid obtained by the first action of conc. H_2SO_4, on further heating loses H_2SO_4 from two molecules, giving $(C_6H_4CH_2)_2$.

***Benzhydrol,** Ph_2CHOH, **secondary.**

This is a colourless solid of definite m.p. boiling with partial decomposition into the ether $(Ph_2CH)_2O$, also solid. In general, it reacts quite normally as a secondary alcohol.

***Triphenyl Carbinol,** Ph_3COH, **tertiary.**

This is a colourless solid of definite m.p. and b.p. In some of its reactions it is quite normal, forming ethers and esters, but its haloid esters behave as salts, dissolving in water with a yellow colour, the soln. evidently containing a triphenylmethyl ion, + of course.

***Saligenin,** $C_6H_4(OH)CH_2OH$ (ortho).

This phenol-alcohol occurs as a glucoside in salicin. It is a colourless solid of definite m.p., sol. in hot water, in alcohol and in ether. It is sol. in alkalis, being a phenol, but is resinified by acids.

On oxidation it gives first salicylaldehyde, then salicylic acid.
With ferric chloride it gives a blue colour.

**Salicin* is a white solid of definite m.p., with a bitter alkaloidal taste. It is sol. in hot water and in organic solvents.

It hydrolyses into glucose, resinified by alkalis, and saligenin, resinified by acids; so that the reagent used depends on which constituent is required.

On oxidation with hydrolysis it should give salicylic acid.

Try with $KMnO_4$ and NaOH, boiling. Identify the acid as usual.

It does not react with ferric chloride.

**Populin* is the benzoyl ester of salicin, on the CH_2OH group. The benzoyl group is separated on hydrolysis.

Benzyl Haloids, *e.g.* **Chloride,** $C_6H_5CH_2Cl$.

These are colourless liquids with powerful tear-exciting odour (the bromide is much worse than the chloride); this is very characteristic. Their b.ps. are high, and they are insol. in water, sol. in organic solvents.

I. *a.* Benzyl chloride burns with a very smoky flame.

c. Wet way oxidation is preceded by hydrolysis as usual. Apply the method given under benzyl alcohol.

II. *a.* Dry way reduction gives toluene.

f. Find the halogen in it as usual, Na and alcohol.

V. *a.* Halogen may replace H of the ring, forming *e.g.* chlorbenzyl chloride.

For conditions see under Hydrocarbons.

VII. 1. *b.* Ethers are obtained by the usual method, by action of RONa.

3. *c.* Esters similarly, by using silver salt of acid.

IX. *a.* Water hydrolyses them but slowly.

b. Alkalis require long boiling.

X. *c.* Sodium eliminates halogen from two molecules, forming hydrocarbons (Fittig).

XIII. They give phenylnitromethane with silver nitrite.

They give benzylamine with ammonia.

k. With benzene in presence of $AlCl_3$ they give diphenylmethane.

Benzyl Esters, *e.g.* **acetate, benzoate,** hydrolyse perfectly normally.

Benzylamine, $C_6H_5CH_2NH_2$, primary.

This reacts quite like an aliphatic primary amine; for example, it gives the alcohol and nitrogen with nitrous acid.

AROMATIC ALDEHYDES.

Benzaldehyde, C_6H_5HCO.

This is a colourless liquid of characteristic smell, only slightly sol. in and heavier than water, sol. in organic solvents, with definite b.p.

I. *a.* Combustible, burns easily with smoky flame.

c. Wet way oxidation gives, of course, benzoic acid.

Try with alkaline permanganate. Separate and identify the product.

d. Fehling's Soln. has no action on it. See IX. *b.*

e. With Tollens' Reagent it gives the usual silver mirror.

Try these reactions in the usual manner.

II. *f.* Sodium amalgam and water reduce it to benzyl alcohol.

V. *a.* Halogens replace H of the ring.

VI. Phosphorus pentachloride gives benzylidene chloride (*q.v.*), normally.

IX. *b.* It is, of course, not hydrolysable, but conc. KOH, acting on two molecules, converts one into benzyl alcohol the other into benzoic acid (salt).

Mix together 10 gm. of benzaldehyde, 9 gm. of KOH, and 6 c.c. of water in a stoppered bottle. Shake until a permanent emulsion is formed. Stand four hours. Dissolve in the minimum quantity of water. Extract twice with ether. Distil off the ether. Rectify the benzyl alcohol. Precipitate the benzoic from the aq. part by dil. H_2SO_4, filter and recrystallise from hot water.

XIII. *a, b.* It may be sulphonated and nitrated as usual.

XIV. 1. *b.* Instead of forming an addition cpd. with ammonia, it condenses into hydrobenzamide $(C_6H_5HC)_3N_2$.

c. With conc. HCN it behaves normally, forming mandelonitrile, Ph.HCOH.CN, which hydrolyses to mandelic or phenylglycollic acid, Ph.HCOH.COOH.

d. With $NaHSO_3$, the usual addition cpd. is formed. Used in its preparation.

2. *a, b.* The usual condensations with Hydroxylamine and Phenylhydrazine.

Add to a few drops of phenylhydrazine an equal volume of glacial acetic, dilute a little and add a drop of benzaldehyde; the phenylhydrazone crystallises out.

f. It gives no aldehyde resin. See IX. *b.*

g. It slowly acts on Schiff's Reagent, producing the usual colour.

Try this as usual.

It gives condensations with many other bodies; aniline, acetone, etc.

XV. On boiling with alcoholic KCN, two molecules polymerise by a sort of aldol reaction into benzoïn, $C_6H_5HCOH.COC_6H_5$.

Other simple aldehydes having the HCO attached to a ring behave as above.

Salicylaldehyde, HOC_6H_4HCO, **ortho, a phenyl aldehyde.**

This, the essential oil of Spiraea, is a colourless liquid, sol. in water and in alkalis (XII.) volatile in steam, sol. in organic solvents, of definite b.p.

Its reactions are those belonging to its functional groups, OH and HCO.

Thus it gives results quite similar to phenol in Reactions:—

I *a.*; V *a.*, *c.*; VII 2., 4.; VIII; XII *a.*, *b.*, *d.*;

and it gives results quite similar to benzaldehyde in Reactions

I *c.*, *d.*, *e.*, *h.*; II *f.* (product saligenin); IX *b.*; XIV 1. *d.*, 2. *a.*, *b.*, *f.*, *g.*

Carry out the following phenolic reactions :—

Br water, V. *a.* Ferric chloride, XII. *d.*

And the following aldehyde reactions :—

Fehling's Soln. I. *d.*; Tollens' Reagent, I. *e.*; Schiff's Reagent, XIV. 2. *g.*

**Helicin* is the glucoside of Salicylaldehyde. It behaves quite normally.

*Aldehydes, like *phenylacetaldehyde*, $PhCH_2HCO$, react like aliphatic aldehydes.

Benzylidene Chloride, $PhCHCl_2$, may be considered as a haloid ester of benzaldehyde, into which it passes on hydrolysis with water, and it passes into benzoic acid on oxidation, hydrolysis preceding the other action.

It is a thick colourless liquid of acrid smell, insol. in water, miscible with organic solvents, with definite b.p.

With alcohols, amines, etc., it gives benzylidene or benzal derivatives.

Prove that it contains halogen as usual.

Boil with water for a time. Neutralise and test for benzaldehyde.

Aromatic Ketones.

Acetophenone, $C_6H_5COCH_3$.

This is a colourless liquid, of characteristic smell, definite m.p. (low) and b.p., insol. in water, sol. in organic solvents.

Its reactions are quite normal, those for ketones and those for ring cpds. mainly.

I. *a.* It is combustible, burning with a smoky flame.

c. Wet way oxidation : results quite normal, benzoic acid and CO_2 resulting.

Try the effect of acid dichromate.

II. *f.* Reduction with sodium amalgam and water gives secondary alcohol, $C_6H_5,CHOH,CH_3$.

V. *a.* When halogens act on it boiling, they enter the side chain, as with toluene.

VI. Phosphorus pentachloride gives $C_6H_5CCl_2CH_3$, normally.

X. *a.* Elimination of water by conc. H_2SO_4 gives first phenylacetylene, then triphenylbenzene, also quite normal.

XIV. 1. It adds on: *c.* Hydrocyanic acid; *d.* Sodium hydrogen sulphite.

2. It condenses with *a.* Hydroxylamine; *b.* Phenylhydrazine.

j. Like acetone, it reacts with sodium nitroprusside and ammonia.

Try as for acetone.

The oxime undergoes a peculiar transformation with agents like conc. sulphuric, HCl in glacial acetic, phosphorus pentachloride, whereby acetanilide is obtained (Beckmann Transposition).

***Benzophenone,** PhCOPh, is a crystalline solid, existing in two forms of different m.p., that with lower m.p. passing into the other on standing, and this into the unstable one on boiling, *i.e.* the distilled liquid solidifies at the lower m.p. It is insol. in water, sol. in organic solvents.

Its reactions are generally normal. Thus on dry way reduction it gives diphenylmethane, $PhCH_2Ph$, while wet way reduction gives that and also benzhydrol, Ph,CHOH,Ph, and benzpinacone, C_6H_5,COH,COH,C_6H_5. On potash fusion it gives benzoate and benzene. It gives the usual ring replacement reactions and the usual condensations for a ketone.

CHAPTER XVIII.

AROMATIC ACIDS.

a. Carboxyl group directly attached to ring.

MONO-CARBOXY ACIDS.

UNSUBSTITUTED ACIDS AND THEIR DERIVATIVES.

These are colourless solids, of definite m.p. and b.p., very little sol. in cold water, much more sol. in hot; sol. in organic solvents. They show all the type reactions for the ring and for the COOH group.

I. They resist wet way oxidation of ring (benzoic), but not of side-chain, *e.g.* o-toluic gives phthalic acid.

II. *h.* Reduction to aldehyde happens on heating their Ca salts with Ca formate, *e.g.* benzoate gives benzaldehyde. Ketones are obtained when the Ca salts are heated alone; benzoate gives benzophenone.

V. *a.* Halogens replace H of ring; compare the case of benzene.

c. Sodium replaces H of COOH, forming salts, in neutral solvents, of course.

Dissolve benzoic in dry ether and add pieces of sodium.

VII. 3. They form esters in the usual ways, HCl gas being the best condensing agent for the case of acid and alcohol.

4. Acid anhydrides formed from acid chloride and a salt of same or of other acid, the mixed anhydrides in the latter case being unstable on distillation.

VIII. They are not well ionised, *e.g.* are weak acids requiring phenolphthalein as indicator for exact neutralisation point.

VI. Phosphorus halogenides give acid halogenides.

See Preparation of Benzoyl Chloride.

X. *d.* Soda-lime eliminates CO_2 from acid or its salts, giving hydrocarbon.

Mix a little benzoic acid or Na salt with excess of soda lime in an ignition tube fitted with a delivery tube. Heat strongly and collect and identify the benzene as usual (Fig. 1).

XII. *a.* They form salts by reacting with bases, oxides, hydroxides, carbonates.

Dissolve a few gm. of benzoic acid in hot water; add gradually milk of lime, testing with phenolphthalein until alkaline. Evaporate down and let crystallise. Finish as usual.

b. They are removed from these salts by strong mineral acids, and, being insol., are ppd. in cold solns.

To a cold soln. of Na benzoate add dil. H_2SO_4 in excess. Filter off and wash the pp. Finish as usual.

XIII. *a, b.* The acids can be sulphonated and nitrated in the usual way.

Benzoic Acid, C_6H_5COOH, and its **salts.**

This forms colourless plates, with faint characteristic smell, sol. (but not largely) in boiling water, volatile with steam.

I. *a.* Acid combustible, salts partly so, with smoky flame and carbon residue. The acid partly sublimes and partly passes into anhydride of peculiar pungent smell, causing coughing.

Try the effect of heating the acid and salts.

VII. 3. *a*. See Preparation of Ethyl Benzoate.

b. Make ethyl ester from EtOH, sodium benzoate, and conc. sulphuric heated together gently. Note its characteristic smell.

IX. *a*. Sol. salts must be slightly hydrolysed by water, since pure samples are alkaline to the stronger indicators like methyl orange.

Test a few samples, including your own make.

XII. *c*. Formation of insol. salts.

Add ferric chloride to a soln. of a benzoate. A light brown pp. of a basic salt is produced. Acidify with dil. HCl; benzoic acid is ppd. Compare succinates.

Calcium chloride gives no pp.

Benzoic Esters, *e.g.* **Ethyl Benzoate,** $C_6H_5COOC_2H_5$.

These are liquids or solids of pleasant smell, of definite b.p., insol. in water and in aq. solns., sol. in organic solvents, slightly heavier than water.

Their reactions are exactly like those of other esters, with, of course, the particular properties due to the acid, *e.g.* combustibility.

Carry out a hydrolysis of the ethyl ester. Identify products as usual.

Benzoyl Chloride, C_6H_5COCl, as an **acid chloride.**

This is a colourless liquid of unpleasant smell, very irritating to the eyes, with definite b p. It fumes in the air, due to hydrolysis by water vapour.

Its reactions are quite normal, *e.g.* its combustibility.

Hydrolysis by water is rather slow, owing to the insolubility of the acid, but by alkalis it is rapid.

It readily forms esters by the Schotten-Baumann method, applied as usual.

Confirm these points.

Ammonium carbonate gives Benzamide. See this Preparation.

***Benzoic Anhydride** is a solid of definite m.p. and b.p. with normal reaction.

Benzamide, $C_6H_5CONH_2$, or $C_6H_5C(OH)$,NH, **an amide.**

This is a colourless solid, crystallising in pearly plates, with no particular smell, of definite m.p., sol. in hot water and in organic solvents.
Its reactions are generally quite normal. It is not very combustible. It hydrolyses fairly easily into benzoic acid and ammonia.

Boil a sample with NaOH. Identify NH_3, and the acid after neutralising.

Hot soda lime may cause the elimination of water, giving benzonitrile.

Heat with the soda lime; note the smell of PhCN, like nitrobenzene.

Benzonitrile, C_6H_5CN.

This is a colourless oily liquid, smelling like $PhNO_2$ (compare the isocyanide), of definite b.p., insol. in water, sol. in organic solvents.
Reactions generally normal. Combustible, but not very readily.
Hydrolysed slowly by boiling with alkalis or acids (medium conc.) normally.

Hippuric Acid, Benzoylaminoacetic, $C_6H_5CONHCH_2COOH$.

This forms colourless prisms, without smell if pure, slightly sol. in cold water, more sol. in hot, sol. in alcohol, insol. in ether. It has a definite m.p., but decomposes on further heating into HCN, benzonitrile and benzoic acid, etc.

I. *a*. It is combustible, burning with a smoky flame, and leaving carbon.

VII. 3. It forms esters in the usual ways.

IX. *b*, *c*. On boiling with acids or alkalis it gives glycin and benzoic acid.

f. Hot soda lime decomposes it into benzene, ammonia, etc.

Try these two reactions.

XII. *a*. Unlike glycin itself, it forms true salts with the alkalis, very sol. in water. It can decompose carbonates.

b. It is separated from its salts by dil. mineral acids, and ppd., being insol.

c. The sol. salts give a red pp. with ferric chloride.

Try these tests as usual.

SUBSTITUTED BENZOIC ACIDS, AS TYPES OF THE CLASS.

1. **Mono Halogen,** o-, m-, p-, *e.g.* ClC_6H_4COOH.

These are crystalline solids, of definite m.p. and b.p., varying solubility in water, sol. in organic solvents. Salts mostly sol.; Ba salts used in separation of isomers, *o*- most sol. They are stronger acids than the original.

Halogen proved by reduction by Na and alcohol.

Potash fusion (mild) gives hydroxy acid.

2. **Mono-nitro,** o-, m-, p-, $NO_2C_6H_4COOH$.

These are crystalline solids faintly yellow, of definite m.p., only slightly sol. in water. Alkali salts sol. in water. Acids sol. in organic solvents. Stronger acids than original.

Prove acid as usual with alkali and indicator.

Prove nitro group as usual.

3. **Mono-amino,** o- is **Anthranilic acid,** $NH_2C_6H_4COOH$.

A colourless crystalline solid, of definite m.p., sol. in water, sweet taste. A weaker acid than benzoic and, as a primary amine, forming salts with the strong mineral acids. On heating it gives aniline and CO_2. With nitrous acid it gives salicylic acid, but its salts (*e.g.* with HCl) give the diazo reaction.

4. **Mono-Sulphonic,** o-, m-, p-, $HSO_3C_6H_4COOH$.

These, as having both COOH and SO_3H groups, are dibasic acids, giving carboxyl and sulphonyl salts, chlorides, a cyclic anhydride from the ortho, and also a cyclic imide, $C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>NH$. This is the substance called *Saccharin* used as a very powerful artificial sweetening agent. It is difficultly sol. in cold water, acts like an acid, forming imide salts, *e.g.* the very sol. Na salt. Thus it behaves like phthalimide (*q.v.*), and the original acid also resembles phthalic acid (*q.v.*) forming phthaleins.

Hydroxy or Phenol Acids.

Mono-HO-, ortho is **Salicylic Acid,** HOC_6H_4COOH.

This is a colourless solid, crystallising from alcohol in prisms, from hot water in needles, only slightly sol. in cold water; chloroform is the best solvent. The acid has a definite m.p. but decomposes at higher temperatures.

The salts are generally sol. in water and crystalline.

I. *a.* The acid is fairly combustible, burning with a smoky flame. The salts are partly combustible, leaving a carbon residue containing alkali.

Try the acid and the sodium salt.

II. *a.* Heated with zinc dust it gives phenol and benzene.

V. *a.* Bromine water gives a whitish pp. of tribromsalicylic acid.

Apply this test.

c. Sodium can react on the phenol and on the carboxyl groups.

VII. 1. It forms phenolic ethers in the usual way.

3. It forms carboxylic esters in the usual way.

Mix together the acid, methyl alcohol and a little conc. sulphuric acid. Warm gently. Note the smell of the methyl ester.

4. It forms phenolic esters as by the Schotten-Baumann method, *e.g.* acetosalicylic acid $CH_3COOC_6H_4COOH$, called "Aspirin."

VIII. It is not a strong acid, not definitely affecting indicators like methyl-orange.

IX. *a.* Its normal salts are faintly alkaline, being partly hydrolysed. The so-called basic (phenolic) salts are completely hydrolysed as regards that group.

X. *a.* On heating alone it passes largely into phenyl salicylic ester, salol, with elimination of water and CO_2.

d. On heating with soda lime, CO_2 is retained, phenol being set free.

Do this, noting the smell of the phenol.

XII. *a.* It reacts with alkalis, forming normal salts not decomposed by CO_2.

b. These are decomposed by stronger acids, with precipitation of salicylic acid.

Further action by alkalis produces basic phenolic salts, *e.g.* $C_6H_4(ONa)COONa$, which are decomposed by CO_2 or even by water (the soln. being strongly alkaline), forming the normal salt: compare lactates, carbonates.

c. None of the common salicylates are really insol. in water, but on boiling the acid with lime water a pp. of basic Ca salt $C_6H_4CO_2OCa.H_2O$ is obtained.

d. The normal salts give a violet colour with ferric chloride (phenolic).

Try *c.* and *d.* as directed.

XIII. *a.* The acid can be sulphonated in the usual way, giving sulphosalicylic.

b. Similarly for nitration.

Salicylic Esters.

Methyl Salicylate is a colourless liquid of peculiar smell, boiling unchanged, only slightly sol. in water, miscible with other organic liquids.

It is combustible, burning with a smoky flame.

Addition of alkali, KOH, causes a pptn. of $C_6H_4(OK)$-$COOCH_3$. On boiling, this disappears and hydrolysis takes place.

It still gives the usual phenol reaction with ferric chloride.

Note these points practically.

Phenyl Salicylate or **Salol** is a colourless crystalline solid, with a faint smell, of definite m.p. and b.p., insol. in water, sol. in organic solvents. On hydrolysis with KOH it gives phenate and salicylate. Separate thus:—Pass in CO_2; the phenate is decomposed. Extract the phenol with ether. Separate. Evaporate off the ether from each liquid. Identify the phenol. Neutralise the aq. liquid and identify the salicylic acid in it.

Carry out the above.

Salol gives the ferric chloride reaction in alcoholic soln.

Try this.

***Anisic Acid** is p-methoxybenzoic acid. It is a colourless crystalline solid of peculiar smell, of definite m.p. and b.p.

Its reactions are those to be expected from a phenyl-ether-carboxy acid.

As an acid it forms definite salts, esters, etc. These and the acid, when heated with soda lime, give off anisol (*q.v.*).

As an ether it is hydrolysed only by conc. HI or HCl, giving methylhalide, and for the same reason it does not react with ferric chloride.

***Gallic Acid** is a **trihydroxymonocarboxy acid** 3, 4, 5, $(HO)_3C_6H_2COOH$.

It forms fine silky needles, difficultly sol. in cold water, readily in hot, sol. in alcohol and in ether, melting with decomposition into CO_2 and pyrogallol. Its reactions resemble those of that substance, except that it forms more definite salts and these (or the acid) give with ferric chloride a blueblack pp. (ordinary ink). $FeSO_4$ gives no change but the mixture gradually darkens by oxidation into the above. Like pyrogallol it reduces Ag salts and the solns. of its alkali salts gradually become brown in the air by oxidation.

Try the reaction with ferric chloride.

***Tannic Acid** is a colourless or yellowish solid, very sol. in water, less sol. in alcohol, almost insol. in ether, insol. also in salt solns. and ppd. On heating it is converted into pyrogallol, with blackening. Further heating chars it entirely. Boiling with dil. H_2SO_4 converts it into gallic acid, it is therefore the gallate ester (phenolic) of gallic acid; and with ferric chloride it gives reactions similar to this acid. It gives a white pp. with gelatine soln.

Try with ferric chloride and with gelatine soln.

Di-Carboxy Acids.

Phthalic Acid is the ortho acid, $C_6H_4(COOH)_2$.

This is a colourless solid, crystallising in prisms or plates, of definite m.p. (see X.), sol. in cold water, easily in hot, and in alcohol and ether.

There are, of course, two series of alkali salts, normal and acid; these are solids of normal reaction.

I. *a*. It is combustible, but less so than benzoic acid.

b. Acid dichromate oxidises it completely.

II. *h*. Presumably its salts behave normally when heated with formate.

VI. PCl_5 gives acid chloride, possibly of unsymmetrical structure.

$$C_6H_4\begin{cases}-CCl_2 \\ \qquad\quad > O \\ -CO\end{cases}$$

(See succinyl chloride.) This hydrolyses normally with water, etc.

VII. 3. It forms esters, quite in the usual manner—two series. The mono- act as acids (see similar aliphatic esters). The di-esters are oily liquids of high b.p., reacting quite normally.

VIII. It is a stronger acid than benzoic, showing a distinct acid reaction.

Try the usual tests for acidity.

IX. *b*, *c*. The esters are hydrolysed normally with alkalis or acids.

e. On heating the acid or its salts with lime, CO_2 is removed, and either Ca benzoate left or, with excess of lime, benzene itself set free.

Carry out the latter reaction as usual. Identify the benzene.

X. *a*. On heating the acid alone, or with acetyl chloride, it loses water, passing into the anhydride (below). See Succinic Acid.

Heat a quantity of the acid in a porcelain basin on a sandbath. Put over the basin a tall beaker or a wide t.t. The anhydride sublimes into this.

e. Similarly, the NH_4 salts heated in HCl gas eliminate NH_3 etc. and give phthalimide (below).

XII. *a*. The acid decomposes carbonates and reacts with bases generally.

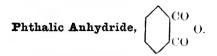
Make a soln. of the sodium salt by neutralising a soln. of the acid in hot water with Na_2CO_3.

b. The acid is separated from its salts by "strong" acids, *e.g.* dil. H_2SO_4, and may be ppd. from conc. solns. or in any case extracted by ether.

Carry out this reaction with the above soln.

c. It forms some insol. salts. Use the above soln. of sodium salt.

Add $BaCl_2$ and a little alcohol: white pp.
Add $FeCl_3$: a reddish brown pp. of basic salt.
} Compare succinic acid.

Phthalic Anhydride,

This forms very long thin needles of sharp acid smell, of definite m.p. and b.p., sol. in water, especially in hot (IX.) sol. in neutral organic solvents.

It reacts in general like the acid of course, but:—

V. *c.* Sodium gives no hydrogen, in neutral solvents.

IX. *a.* On warming with water it passes back into the acid.

b. Similarly alkalis give salts which are sol.

XIII. *j.* With ammonia gas, the anhydride gives phthalimide.

Heated with phenolic bodies and dehydrating agents a condensation into phthaleins results.

Mix a little anhydride with twice as much phenol and a few drops of conc. H_2SO_4. Heat in a t.t. over a sandbath for some time. Let cool, pour into water and make alkaline with NaOH. The crimson colour of phenolphthalein-sodium becomes visible.

Mix a little with resorcinol and heat gently. Pour out, etc., as above. Note the splendid green fluorescence, due to fluorescein.

Repeat with catechol.

Repeat with quinol.

***Phthalimide,** $C_6H_4 < \begin{matrix} CO \\ CO \end{matrix} > NH$ or $C_6H_4 \begin{matrix} \diagup C(NH) \diagdown \\ \diagdown CO \diagup \end{matrix} O$.

This is a colourless solid of definite m.p.

It behaves as a quasi-acid, giving with alcoholic KOH the substance $C_6H_4(CO)_2NK$ which gives pps. with salts of the heavy metals. The silver salt gives ethers with alkyl iodides.

With Br and KOH it gives anthranilic acid (*q.v.*).

On long boiling with alkalis it should hydrolyse to the original acid.

β. Acids with COOH in side-chain are :—

AROMATIC ALIPHATIC ACIDS.

***Phenylacetic** or **alphatoluic acid** is a colourless solid of definite m.p. and b.p. Its reactions correspond to its composition. Thus the action of halogens on it is exactly like their action on toluene.

Chromic acid oxidises it to benzoic acid.

***Phenylpropionic** or **hydrocinnamic acid** resembles the above very closely.

Chromic acid oxidises it to benzoic acid.

***Phenylglycollic** or **Mandelic acid** resembles lactic acid, existing like it in three stereoisomeric forms. Oxidation gives first benzoylformic or phenyl-glyoxylic Ph,CO,COOH, then benzoic acid.

Amygdalin, $C_{20}H_{27}NO_{11}$ 3 aq. is the maltoside of the nitrile of this acid, decomposing on hydrolysis into benzaldehyde, HCN, and glucose (2 mols.).

UNSATURATED AROMATIC ALIPHATIC ACIDS.

Cinnamic or **phenylacrylic acid,** $C_6H_4CH:CH.COOH$.

This is a colourless solid, crystallising in needles or plates, with definite m.p. and b.p., very slightly sol. in cold water, readily in hot, sol. in organic solvents. Its salts are solids, some easily sol. in water.

I. *a*. The acid is fairly combustible, burning with smoky flame.

b. Acid dichromate gives benzaldehyde and oxalic acids, also some benzoic acid.

Confirm this statement.

II. *f*. With nasc. hydrogen (sodium amalgam and water) hydrocinnamic is obtained.

See Preparation of Hydrocinnamic Acid.

h. Cinnamates heated with formates give cinnamaldehyde.

III. *a*. Being unsaturated it adds on bromine.

Warm the acid with a little bromine water. It is decolorised.

VI. PCl_5 gives cinnamoyl chloride: normally.

VII. 3. It forms esters quite in a normal manner.

Warm with some ethyl alcohol, and conc. H_2SO_4. Note smell of ester.

VIII. It is not a strong acid.

Test a soln. in alcohol or hot water.

IX. *a*. Solns. of the alkali salts react slightly alkaline, therefore are hydrolysed.

b, *c*. The acid chloride and the esters are hydrolysed normally.

e. Gentle potash fusion produces benzoate and acetate.

Strong heating with soda lime produces styrolene: quite normally.

Carry out this as usual, collect the distillate; prove unsaturated.

XII. *a*. The acid decomposes carbonates and reacts with bases generally.

Make a sol. salt as for phthalic.

b. It is separated from its salts by dil. H_2SO_4 and ppd.

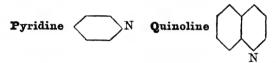
c. The sol. salts give a yellowish pp. with ferric chloride.

Confirm these two reactions, using the above soln.

XIII. *a*, *b*. The acid can be sulphonated and nitrated directly.

CHAPTER XIX.

HETERO-CYCLIC BASES.

Simple Rings.

These bases resemble in some ways the simple aromatic amines (tertiary), in other ways the much more complex alkaloids, q.v.

P. is a colourless liquid of characteristic unpleasant smell, and with definite low b.p. Miscible with water.	Q. is a liquid generally yellow to brown, of peculiar smell and definite high b.p. Slightly sol. in water.

Miscible with ordinary organic solvents.

Salts often crystalline, generally deliquescent and very soluble.

I. *a.* Nearly incombustible.	Not easily combustible.
Try both as usual.	
Resists wet way oxidation.	*b.*, *g.* CrO_3 and HNO_3 have no action. *c.* Alkaline $KMnO_4$ destroys Bz. ring giving pyridine-di-COOH acid.

The side-chains in their homologues are oxidised to carboxyl groups.

II. *j.* Conc. HI hot gives pentane.	
Milder agents give hydro-derivatives.	Here hydroquinolines to deca-hydro result.

V. *a*. Halogens cause substitution with some difficulty.

c. Sodium has no action, since they are tertiary bases.

VII. 2. Being tertiary bases, alkyl iodides are first added on, forming the quaternary iodides. On adding silver hydroxide the hydroxides result, but they are unstable and soon decompose.

Heat a few drops of pyridine with an equal quantity of MeI for a few minutes. Then add a small piece KOH and heat again; note smell.	Mix equal quantities of quinoline and MeI, warm gently. Let cool. Yellow crystals of quaternary iodide separate.

4. Being tertiary bases, they cannot be acylated.

VIII. Their solns. in water are rather alkaline, indicating ionisation but:—

IX. *a*. Their salts react acid, therefore are hydrolysed.

Confirm these statements.

XI. *a*. They form salts by direct union with acids, sometimes organic, but:—

b. They are displaced from these by strong bases—alkalis.

c. These aq. solns. pp. the hydroxides of most heavy metals from salts.

Cautiously mix medium conc. sulphuric with a few c.c. of each, avoiding excess of acid. Note if a sulphate will crystallise out.

To part of this add H_2PtCl_6, an orange yellow pp. $P_2H_2PtCl_6$ is formed. Boil, it dissolves to come down as yellow P_2PtCl_4.	To part of this add $K_2Cr_2O_7$ and shake, a yellow pp. of $Q_2H_2Cr_2O_7$ is produced.

Add solns. of the bases to ferric chloride, red $Fe(OH)_3$ is ppd.

XIII. *a*, *b*. They are sulphonated and nitrated with difficulty.

c. They do not react with nitrous acid; compare aromatic tertiary bases.

The Alkaloids.

To this class were formerly assigned all nitrogenous bodies from natural sources, of basic character, and of originally unknown complex structure. But the latter in many cases has been determined more or less completely, so that the substances can now be classified in the proper place. This in some cases is in the aliphatic group, *e.g.* caffeine, etc., and the ptomaïnes or corpse alkaloids. Others by their decompositions are related to pyridine or quinoline.

Of these latter aromatic alkaloids, some, containing no oxygen, are liquid and volatile without decomposition, *e.g.* coniine $C_8H_{17}N$ and nicotine $C_{10}H_{14}N_2$; those containing oxygen are generally solids of definite m.p. but decompose at higher temperatures.

They are amines of various orders, mono-, di-, etc., tertiary, less frequently secondary or primary, and act as bases, mono-, di-, etc. acidic.

They may be tabulated as follows:—

Name.	Formula.	Amine.	Order.	Acid.	OH groups.	Ether.	Other groups.
Morphine ...	$C_{17}H_{19}NO_3$	Mono	Terty.	Mono	One alc. One phen.	—	?
Cinchonine ...	$C_{19}H_{22}N_2O$	Di	Terty.	Di	One alc.	—	One Me
Quinine ...	$C_{20}H_{24}N_2O_2$	Di	Terty.	Di	One alc.	One (OMe)	One Me.
Strychnine ...	$C_{21}H_{22}N_2O_2$	Di	{ Terty. { Quatern.	Mono	?	—	?
Brucine ...	$C_{23}H_{26}N_2O_4$	Di	{ Terty. { Quatern.	Mono	?	Two (OMe)	?

They react as follows :—

XI. *a.* They form salts etc., of solubility varying for each alkaloid, with the following alkaloid precipitants.

1. Chloroplatinic acid: yellow, often crystalline, insol. in alc. and therefore resembling $(NH_4)_2PtCl_6$. From these the alkaloid is obtained by adding NaOH soln. and extracting with the proper solvent.

2. Potassium Mercuriodide: white or yellowish white pps. insol. in dil. HCl. To extract: rub up pp. with $SnCl_2Aq$ and excess of KOH. Extract with the appropriate solvent.

3. Phosphomolybdic Acid: light to brownish-yellow pps. like the NH_4 cpd. insol. in dil. acids, except H_3PO_4. Add alkali and extract as above.

4. Phosphotungstic Acid, or Na salt: results quite similar to above, 3.

5. Iodine in KI, Aq.: brown flocculent pps. in presence of H_2SO_4. Add $Na_2S_2O_3$ or H_2SO_3 in excess, make alkaline, extract as usual.

6. Tannic Acid } also precipitate
   Picric Acid } many alkaloids.

   Try 2, 3, 5, using Quinine.

b. The alkaloids to be considered here may be classified thus :—

1. Those ppd. from salts by NaOH Aq. in excess :—

   Strychnine, Brucine, Quinine, Cinchonine.

2. Those ppd. from salts by $NaHCO_3$:—

   Quinine, Cinchonine, Morphine.

3. Not ppd. from salts by $NaHCO_3$:—

   Strychnine.

Morphine, $C_{17}H_{19}NO_3,H_2O$: from opium.

This crystallises from alcohol in small prisms, nearly insol. in cold water, slightly in hot, sol. in hot alcohol, insol. in ether and in $CHCl_3$. Hot amyl alcohol is the best solvent. Morphine melts with some decomposition.

Its salts are sol. in water and in alcohol, and are crystalline solids, *e.g.* Morphine HCl, 3 aq.

I. *a.* It is only slightly combustible.

Morphine is oxidised by iodic acid, liberating iodine.

Add soln. to HIO_3 Aq.; identify iodine as usual.

Various other colour reactions are probably oxidation.

VII. Morphine has two OH groups; either or both of these can be alkylated and acylated by the usual methods.

VIII. Its soln. has an alkaline reaction, but its salts react acid; therefore they must be hydrolysed in water to some extent.

IX. Its ethers and esters (above, VII.) can be hydrolysed by the usual methods.

c. Heated with soda lime, morphine gives NH_3.

XI. *a.* Morphine dissolves in dil. acids, forming salts which will crystallise.

b. Na_2CO_3, $NaHCO_3$ and ammonia pp. the base, sol. in the last in great excess.

XII. *d.* Morphine, as a phenol, dissolves in NaOH, and gives a colour with $FeCl_3$.

Add ferric chloride to a soln. of morphine base; bluish green colour.

Confirm reactions VIII., XI., and XII.

Quinine, $C_{20}H_{24}N_2O_2$, $3H_2O$: from cinchona bark.

This crystallises from alcohol and from ether in silky needles, sparingly sol. in water, readily in benzene and in petroleum; the best solvent is chloroform. The base has a definite m.p.

Its salts are crystalline, and most are sol. in water. There are two classes, monoacid and diacid, *e.g.* quinine HCl, 2 aq. quinine H_2SO_4, 8 aq. (long needles).

I. *a*. Quinine burns with a smoky flame, leaving much carbon.

b. Potassium dichromate and conc. H_2SO_4 produce a grass green colour.

k. Br Aq., not too strong, then a little NH_3, Aq. gives a bright green colour or pp. This is the "Thalleioquin" Reaction.

Try these.

VII. Having one OH group, quinine forms ethers and esters as usual.

VIII. Quinine soln. is strongly alkaline to litmus, being a strong base. The diacid salts are hydrolysed partly, for they react acid.

IX. *d*. Hot conc. HI replaces the (OMe) group by OH—Zeisel's Reaction.

XI. *a*. Quinine dissolves easily in acids, but,
b. is ppd. from these by alkalis. The salts dissolve in excess of acid and the solns. in oxyacids show a beautiful blue fluorescence.

Confirm these results.

Dissolve quinine sulphate in acetic, add an equal bulk of alcohol, then alcoholic iodine soln. Warm and let stand. "Iodoquinine" is ppd. in black crystals with golden lustre.

Cinchonine, $C_{19}H_{22}N_2O$, forms colourless needles of definite m.p. sublimable in a current of hydrogen, insol. in water, nearly so in ether, slightly sol. in $CHCl_3$, more easily in alcohol. Most of its salts are sol. in water.

It reacts like quinine, but differs from it as follows:—

It gives no colour reactions when tested as quinine. Its salt solns. are hardly at all fluorescent.

Strychnine, $C_{21}H_{22}N_2O_2$: from Nux Vomica, etc.

This crystallises in rhombic prisms, of definite m.p. and volatile in a high vacuum, nearly insol. in water, in alcohol, and in ether, most sol. in $CHCl_3$.

Its salts are generally fairly sol., some only slightly so. There are two sulphates, S, H_2SO_4 and S_2, H_2SO_4 ; the chloride is S.HCl, 2 aq.

I. *a*. It burns as usual for such cpds. leaving much carbon.

b. With $K_2Cr_2O_7$ and conc. H_2SO_4 it gives an intense purple colour.

c. With conc. HNO_3 and a little $KClO_3$ a scarlet colour.

Try these colour tests.

VIII. Its solns. react alkaline, but the salts are partly hydrolysed.

XI. It gives the usual basic reactions. It is ppd. by NaOH not by carbonates.

Confirm VIII. and XI.

Brucine, $C_{23}H_{26}N_2O_2$ 4 aq. : source as for strychnine.

This crystallises in prisms or tables of definite m.p. when anhydrous, insol. in ether, easily in absolute alcohol and in $CHCl_3$, sparingly sol. in water.

The salts, *e.g.* B.HCl, $B_2H_2SO_4$, are crystalline and most of them are sol. in water.

It reacts in general like strychnine but $K_2Cr_2O_7$ and conc. H_2SO_4 give a red brown colour. Conc. HNO_3 gives an intense red colour; on evaporating off the acid and adding $SnCl_2$, an intense violet colour is obtained.

Confirm the statements as to colour reactions.

The two (OMe) groups are replaced by 2OH by heating with conc. HI.

CHAPTER XX.

SYSTEMATIC SCHEME FOR IDENTIFICATION OF UNKNOWN SUBSTANCES.

SECTION I.—SUBSTANCE NOT MIXTURES.

The following tests have been arranged in such an order that at any particular point as much has been discovered about the substance under examination as possible, though it may not have been identified.

The results given by some of the earlier tests are only indications, not proofs, and when a decided indication of any kind has been obtained it is allowable to diverge to confirmatory or more conclusive tests, as given in the cross references, but the examination should thereafter be resumed at the point on the "main line" from which the divergence was made.

The Roman numerals, etc., here refer only to this systematic scheme.

ORDER OF TESTS.

Test I.	...		Physical properties, etc.
Test II.	...	A.	Ignition in open.
		B.	,, ,, closed tube.
Test III.	...		Conc. sulphuric acid.
Test IV.	...		Soda-lime.
Test V.	...		Water.
Test VI.	...		Caustic Soda.
Test VII.	...	A.	Hydrolysis, alkaline.
		B.	,, acid.
Test VIII.	...	A.	Oxidation, dichromate.
		B.	,, permanganate.
		C.	,, Fehling's Soln.
		D.	,, Silver Soln.

Test IX.	...	A.	Reduction, wet way.
		B.	,, dry way.
Test X.	...	A.	Esterification.
		B.	Acylation.
Test XI.	...		Ferric Chloride.
Test XII.	...		Acids, precipitation of.
Test XIII.	...		Aldehyde and Ketone reactions.
Test XIV.	...		Isocyanide reaction.
Test XV.	...		Nitrous acid.
Test XVI.	...		Potash fusion.
Test XVII.	...		Alkaloids: tests.
Test XVIII.	...		Nitric acid.
Test XIX.	...		Unsaturation. Acetylenes.
Test XX.	...		Tests for elements.

I. PHYSICAL PROPERTIES, Etc.

Observe the physical state, smell, taste (cautiously), of the substance. Compare results with the brief account given below and draw your conclusions.

Physical Condition.

Solids (= S).—All metallic salts of carboxy- and sulphono-acids; most metallic salts of quasi-acids, *i.e.* of phenoloid cpds. and aliphatic enolic cpds.; metallic cpds. of imides, amides, imines, and amines; alkylates.

Common dicarboxy-acids, aliphatic and aromatic; aromatic mono-carboxy-acids and hydroxy-carboxy-acids; also acid amides except formamide.

Phenol and p-cresol, dihydroxy-phenoloid cpds., the naphthols, quinones, most esters of phenolic cpds., substitution derivatives of all these.

Diphenylamine, p-toluidine, diamines; inorganic salts of all primary aromatic amines (some salts of secondary and tertiary amines do not crystallise).

Inorganic salts of all aliphatic amines; (some are very deliquescent).

Urethanes; methyl oxalate, citrate and tartrate; some esters of polyalcohols, *e.g.* fats.

Naphthalene, anthracene, phenanthrene.
Oxygenated alkaloids and their salts.

Liquids (= L).—Lower alcohols, aldehydes, and ketones, aliphatic and aromatic.
Lower aliphatic acids.
Most esters of mono-alcohols, with all kinds of acids.
Most nitrogen bases, monamines, containing no oxygen.
Lower aromatic hydro-carbons and their simple mono- halo- (except iodo-) and mono-nitro derivatives, except p-nitrotoluene.
Most ethers, acid chlorides, and nitriles, aliphatic and aromatic; aliphatic mono-acid anhydrides.

Gases (= G).—Methane to butane; $C(CH_3)_4$; CO, C_3O_2, CO_2; CH_3Cl, C_2H_5Cl, CH_3Br; C_2N_2: H_2CO; CH_3OCH_3.

Smells, characteristic.

Spirituous: lower aliphatic alcohols (amyl characteristic).
Ethereal: lower aliphatic ethers.
Fruity: many esters of all kinds.
Ammonia-like: aliphatic amines; some of tertiaries are "fishy."
Phenolic: most aromatic mono- hydroxy-cpds., and some derivatives of these.
Aniline-like: most aromatic amines and some of their derivatives.
Petroleum-like: most hydrocarbons (naphthalene characteristic).
Acid: lower aliphatic acids, acid halides and anhydrides, including aromatic.
Others are—aromatic mono-nitro-cpds: quinones; isocyanides; and the sweet ethereal smell of aliphatic haloid cpds., from which iodo-cpds. diverge rather.

Taste.

Experiment with caution, and use small quantities only.
Aromatic acids are not always sour, some not at all, *e.g.* benzoic. Most other acids are strong enough to show this evidence.
Sweet substs. are not always sugars; compare saccharin, lactose, resorcin.
Bitter substs. may be alkaloids, but not always; compare picric acid, salicin, quinine.

II. IGNITION TEST.

The indications given by this test are too numerous to be very characteristic, but the more negative results are useful, and the nature of the combustion gives evidence for Aromatic cpds., while its extent suggests the presence or absence of metals.

A. *a.* **Heat the substance on a piece of thin porcelain** (a crucible lid or a piece of a basin), **or,** if reducible metals (Gs. I. and II. and Zn.) are known to be absent, **on platinum foil.**

1. The subst. volatilises, leaving little or no residue.

a. The vapour is not inflammable:—	L. Some polyhaloid cpds., *e.g.* CCl_4. See VII A., IX A. S. Solid polyhaloid cpds. See IX A.
b. The vapours burn with non-luminous flame:—	L. Methyl and ethyl alcohols, glycerol, acetic and formic acids, acetaldehyde, formaldehyde from derivatives, carbon disulphide. See these.[1] S. Flame of CO from oxalic acid, oxamide, methyl oxalate. See these.
c. The vapours burn with luminous flame:—	L. Higher alcohols and aldehydes, lower ketones and ethers, lower esters of lower alcohols, lower aliphatic amines. See these. S. Salts of aliphatic amines. See these.
d. The vapours burn with smoky flame:—	L. Higher aliphatic cpds. of various kinds, aromatic hydrocarbons and amines, mono-nitro cpds. (fiercely), esters, most common halogen cpds. S. Aromatic hydrocarbons, *e.g.* naphthalene, most phenolic cpds. and quinones, aromatic acids in general and their solid derivatives, salts of aromatic amines, solid amines, solid mono-nitro cpds. (fiercely). See these.

[1] *i.e.* refer to these in the general description in the previous part of book. So all through this Systematic Scheme.

2. The subst. leaves a residue, possibly after melting.

a. The vapour is not inflammable (excluding steam):—	L. Mixtures containing substs. under 1 *a*. S. Carbonates, cyanates (see VII B., IV), and some other salts of metals.	
b. The vapour burns with a non-luminous flame:—	L. Mixtures containing substs. under 1 *b*.	
	Esters of lower alcohols with complex aliphatic acids. S. Bright-blue flame of CO from oxalates, III., XII. Peachbloom flame of C_2N_2 from cyanides of Hg, Ag. III. Blue flame of H_2CO from paraformaldehyde, XIII. Blue flame of CH_3HCO from acetaldehyde addition cpds., XIII. Blue flame from sugars; Starch VII B.; Cellulose VII B., etc.	Residue: black, carbon, etc.
c. The vapours burn with luminous flame:—	L. Mixtures with substs. under 1. *c*. L.S. Higher esters of more complex aliphatic acids. S. Many aliphatic cpds.; higher hydrocarbons; some sugars; some aliphatic esters; some polyhydroxybenzenes.	Black carbon residue.
	Ethylene from alkylates and alkylsulphates (with SO_2) VII A, III, XII. Ketones from their addition products, VI, VIII A., XIII.	

<table>
<tr><td>d. The vapours burn with a smoky flame :—</td><td>L. Mixtures with subst. under 1. d.

L.S. Highest aliphatic hydrocarbons ; and complex esters like fats and oils.
Most aromatic cpds., e.g. hydrocarbons like anthracene.
Nitro cpds. (fiercely) ; amines and their derivatives, including certain salts, hydrazines and their salts, acids and their salts, alkaloids and their salts.</td><td>Residue : black, carbon.</td></tr>
</table>

3. Nature of Ignition Residue :—

<table>
<tr><td>a. Black, carbonaceous, more or less completely burnt off on long heating, especially on platinum foil :—</td><td colspan="2">Many cpds., aliphatic (less common) and aromatic ; see above, 2.</td></tr>
<tr><td>b. Black or coloured, not wholly carbonaceous, fixed, i.e. not burnt off on prolonged heating :—</td><td>Various reduced metals, Pt, Ag, Cu (red), Pb beads.
Lower oxides of, e.g. Fe, Mn, Cu (red).</td><td>From organic salts of these, XI, XII.</td></tr>
<tr><td>c. Grey to white, fixed on further heating :—</td><td>Carbonates of alkalis.
Carbonates or oxides of alkaline earths and Mg.</td><td>From organic salts of these, XI, XII.</td></tr>
<tr><td></td><td colspan="2">Sulphates of these, from alkylsulphates VII A. and arylsulphonates XVI.
Sulphides of heavy metals from alkylsulphates and arylsulphonates (reduction by carbon).</td></tr>
</table>

But in presence of sulphur, it is difficult to burn off all carbon.

4. Reaction of Ignition Residue:—

β. **Wet the residue with a drop of water, smell it, and test with litmus.**

This often gives characteristic evidence as to the nature of inorganic constituents as follows:—

a. The reaction is neutral:—	Sulphates of alkalis and of alkaline earths or Mg, sulphides of heavy metals; from alkylsulphates or arylsulphonates of these. VII A., XVI. Carbonates of alkaline earths (may pass into oxides) from organic salts.
b. The reaction is alkaline:—	Carbonates of alkalis and oxides of alkaline earths and Mg, from organic salts of these. XI, XII. Sulphides of these by reduction of alkylsulphates and arylsulphonates.
c. The reaction is acid:—	Salts of the less volatile inorganic acids, *e.g.* phosphates. Arylsulphonates and salts of such ester acids as alkylsulphuric, etc., may leave acid salts of alkalis. VII A., XII.

Confirm carbonates as usual, and sulphides (smell of H_2S by adding a drop of dil. HCl).

B. Heat some O.S. in an ignition tube.

This is supplementary to the Test II A.

Results often repeat those of II A. but, of course, charring is more frequent and the carbon cannot be burnt off.

Characteristic smells may often be observed:—

a. Ammoniacal: NH_4 salts, amides, cyanides, cyanates, urethanes, in these last four cases by hydrolysis by water present; lower aliphatic amines, primary, and their salts.

b. Tarry: aromatic cpds. chiefly; some others.

c. "Burnt feathers": complex nitrogenous cpds.

d. "Burnt sugar": sugars, tartrates, some others.

e. Sulphurous (SO_2): sulphates, alkylsulphates, bisulphites.
f. Phenolic: aromatic HO-cpds., phenates, salicylates, etc.
g. Cyanogen: cyanides of heavy reducible metals, *e.g.* Ag, Hg.
h. "Sulphone": arylsulphonic cpds.

Deflagration may happen in cases of:—

Nitrates of organic bases, *e.g.* urea nitrate, aniline nitrate; some nitro cpds., especially polynitro-, *e.g.* dinitrobenzene, nitrophenols and their salts, nitronaphthols, and, of course, picric acid.

Explosion may happen in cases of:—

Some salts of nitrophenolic cpds., especially picrates. Silver oxalate. Diazo-cpds. A number of other unstable cpds.

III. REACTION WITH CONC. SULPHURIC ACID.

To obtain useful results with this test, attention to the rate of heating and to intermediate occurrences are both very necessary, as well as judgment in observation and in inference.

Mix a little of O.S. with excess of conc. sulphuric in a t.t. Warm, gently at first, noting the effect at intervals as the temperature rises, until white fumes of the acid are evolved.

1. The subst. remains immiscible or unacted upon.	L.S. Aliphatic saturated hydrocarbons. XIX.
2. The subst. dissolves slowly, without violent action.	*a.* L.S. Aromatic hydrocarbons and their halo-, nitro-, sulphono-, derivatives, acids, etc. All dissolve by sulphonation. See XVIII, IX A., XVI, etc. *b.* G.L.S. Unsaturated (olefinic and acetylenic) cpds. dissolve, forming alkyl and arylalkyl and alkylidene, etc., sulphuric acids, by addition. In these cases there may be more or less blackening, *i.e.* charring. *Boil the mixture with water, test for alcohol and for aldehyde.* See VIII A., XIII.

c. L.S. Aliphatic haloid esters dissolve, iodo cpds. give free iodine.

d. L.S. Acetic and higher acids of that group dissolve (sulphonation ?).

e. L. Aliphatic ketones give viscid condensation products, with much charring; finally aromatic hydrocarbons result. See these and XIII.

f. L.S. Certain esters, amides and nitriles, aliphatic and aromatic, dissolve by hydrolysis.

g. Starch and cellulose dissolve as sulphate esters. VII B.

Uric acid and salts dissolve unchanged, the acid crystallising out on dilution.

h. L.S. Aromatic HO-cpds., *e.g.* phenols, dissolve very easily. See XI, XVI.

3. The subst. mixes and reacts rather violently.

a. L. Aliphatic and aromatic alcohols form sulphuric esteracids. See VII A.

The alcohols from fusel oil give also a red colour and a characteristic smell.

b. L. Aliphatic ethers give alkylsulphates, at ordinary or lower temperatures.

c. L. Aliphatic aldehydes polymerise into viscid substances. XIV.

d. L. Aliphatic amines, L.S. aromatic amines and hydrazines form sulphates, sulphonation following with the aromatic cpds. See VI, XVI, XIV, VIII C.

4. The subst. dissolves, with more or less charring due to dehydration.

a. Succinates become yellow only: Citrates yellow to brown. Lactates blacken soon: tartrates at once. See all these and XII.

b. Sucrose blackens at once, VII B.: glucose, levulose, lactose, *pure* specimens only after some time. See all these and VIII C. D.

5. The subst. dissolves more or less rapidly, evolving gases. But if charring occurs, the evolution of CO_2 or of SO_2 gives no useful evidence.

a. Carbon dioxide only: carbonates, carbamates, *i.e.* urethanes urea. IV, VII.

Carbon dioxide with some cyanic acid smelling like SO_2: cyanates. IV, VII.

b. Sulphur dioxide only: bisulphite cpds. of aldehydes and ketones, XIII: (on strong heating) alkylsulphates, arylsulphonates. XVI.

Sulphur dioxide and a yellow pp.: thiocyanates. XI.

c. Carbon monoxide only: formates, VIII D., IX; citrates, XII; lactates (with less conc. sulphuric, these last also give acetaldehyde, XIII).

d. Carbon monoxide and dioxide: Oxalates, XII; Citrates, on long heating, XII.

e. Ethylene and some SO_2: alkylsulphates, if not overheated. VII, XII.

f. Volatile inorganic acids—HNO_3, halogen acids, or decomposition products of these, XII; from salts of these: indicating the presence of organic bases—amines, XI, XIV, XV; hydrazines, XIII C., XI; urea, etc., VII.

IV. REACTION WITH SODA LIME.

The indications given by this test can often be obtained more completely and conclusively by other tests. The action is, in general, the removal of acid anhydrides such as CO_2, SO_2, SO_3. This in general will leave hydrocarbons, hydroxy-, or amino-cpds. Sometimes HX is eliminated, leaving unsaturated bodies. See Hydrolysis, VII A.: Potash Fusion, XVI.

Mix a little of the subst. with finely ground soda lime and put into a hard glass t.t. Nearly fill the t.t. with coarser soda lime. Fit a delivery tube passing into a t.t. standing in cold water. Support the t.t. in a horizontal

position and heat strongly, keeping the soda lime near the mouth of the tube as hot as possible, any evolved vapours passing over this.

1. Salts of amines, aliphatic and aromatic, leave their acid if inorganic, the amines passing off unchanged or decomposing so as to give ammonia. VIII A., XV.

2. Inorganic salts of hydrazines leave the acid. The bases decompose into amines behaving as above, and ammonia (smell).

3. Aromatic ring haloid cpds. mainly distil off unchanged. See IX A.

4. Inorganic aliphatic esters, including haloid, may undergo hydrolysis, giving alcohol and salt, or, eliminating acid, give unsaturated cpd.

   Pass the gas, etc., through hot alkaline permanganate. See VIII B.

5. Aromatic nitro-cpds. may be reduced so as to give ammonia. See IX A.

6. Aliphatic aldehydes give aldehyde resin. See these and VI 6. *b*.

7. Carbohydrates are completely decomposed, into products of peculiar smell.

8. *a*. Unsubstituted aliphatic acids and their salts lose CO_2, evolving saturated hydrocarbon.

   Test the evolved subst. with hot alkaline permanganate: not reduced.

   b. Formates and oxalates should give hydrogen, oxalates possibly also CO.

   Identify these by their flame, etc. VIII D., XI, XII.

   c. Aromatic acids and their carboxy derivations similarly give hydrocarbon. XI.

   Identify the aromatic hydrocarbon by XVIII.

9. *a*. Amides and nitriles give hydrocarbon and ammonia. XIX, XVIII.

Benzamide is also partly dehydrated, giving benzonitril, smelling like $PhNO_2$.

b. Metallic cyanides evolve ammonia by hydrolysis, so also do cyanates. VII.

c. Amino-acids evolve ammonia and hydrocarbons. Urethanes give also alcohol.

10. Acylamines are hydrolysed to acid (8) and amine (1). VII.

11. *a*. Substituted cpds. in general give the reaction for both parts, *e.g.* haloacids behave as acid (8) and haloid ester (4).

b. HO-acids lose CO_2, evolving HO cpd.—alcohol, VIII. A, X A., or phenol, XI.

·13. Polyhydroxy-aromatic cpds. often give some phenol. XI.

14. Sulphonates may undergo Hydrolysis. See XVI.

V. REACTION WITH WATER.

A. For Solubility.

Add the subst. little by little, to a quantity of water in a t.t. Close the t.t. and shake up well. Then warm the mixture to boiling.

1. The subst. reacts more or less violently, producing acid fumes.	Acid chlorides, etc., of aliphatic carboxy-acids, aromatic acid chlorides act less violently. Sulphonyl chlorides react slowly even on boiling. See X A., XI, XII. Identify halogen acid as usual. Acid anhydrides act less violently, and give no fumes. See X A., XI, XII.
2. The subst. is perfectly miscible.	L. Lower aliphatic monoalcohols and their aldehydes, lower amines, acids up to 3-carbon, polyhydroxy cpds., *e.g.* glycol, glycerol, lactic acid.

3. The subst. dissolves to a greater or less extent, with a higher limit.	L. Higher members of series in 2 above. Lower ethers and ketones. Many aliphatic esters except those of higher acids with higher alcohols, especially polyhydroxy, *i.e.* oils. Aromatic esters of lower alcohols, slightly.
	L.S. Lower aromatic amines especially primary; aromatic HO-cpds. phenols, etc., especially if polyhydroxy; naphthols, only in hot; ethers and esters of these only slightly sol. in hot; many substitution derivatives of these.
	L.S. Aliphatic HO-substituted cpds. aldehydes, ketones, acids, especially polyhydroxy, solubility increasing with number of OH groups, *e.g.* sugars.
	S. Many inorganic salts of amines of all classes. Lower aliphatic amides. Aromatic amides, slightly in hot. Most salts of sulphonic acids, many salts of carboxy acids.
4. The subst. is practically immiscible or insoluble.	G.L.S. Hydrocarbons of all classes, except lowest aliphatic unsaturated (gases).
	L.S. Simple halo-substituted derivatives, mono- and poly-, also aromatic simple nitro-cpds. mono- and poly-. Complex esters like fats and oils.

B. Test whether Acid, Alkaline or Neutral.

Add small quantities of blue, and of red litmus soln. to part of this aqueous soln.

1. The blue litmus becomes red: subst. has acid reaction in soln.	L.S. Alkylsulphuric and other inorganic esteracids; sulphonic acids, aromatic and aliphatic; some monocarboxy aliphatic acids and their halo-substitution derivatives; and some HO-acids; also the acid halides and anhydrides of the former of course; some di- and tri-carboxy acids, mostly aliphatic. Some easily hydrolysed esters of these acids, *e.g.* methyl oxalate. Most salts of aromatic amines; because of hydrolysis.
2. The red litmus becomes blue: subst. has alkaline reaction in soln.	S. Alkali and alkaline earth salts of aliphatic carboxy acids and of most aromatic carboxy acids; by hydrolysis. Alkylates, phenates, naphtholates, etc.; by hydrolysis. L.S. Most aliphatic amines, a few aromatic amines, some of the commoner alkaloids.
3. There is no definite reaction in either case: subst. is neutral in soln. to litmus as indicator. See VI. B.	S. Salts of strong organic acids—alkylsulphates and salts of other inorganic ester acids, oxalates, sulphonates, salts of halosubstituted aliphatic acids, some salts of quasi-acids. L.S. Many other sol. substs. not ionised in soln., *e.g.* esters, amides, sugars, aldehydes, alcohols, ketones, etc.

VI. TEST WITH SODIUM HYDROXIDE.

In this test the presence of acids is confirmed and that of bases is indicated, while some of the results anticipate those of a formal hydrolysis, even so far as to render that unnecessary.

a. **Add a little of the subst. to NaOH soln. in a t.t., warming gently.**

1. The subst. is immiscible or insol.	*a*. All aliphatic and aromatic hydrocarbons; simple haloid derivatives, mono- and poly-; simple amines and hydrazines; simple aromatic nitro-cpds., mono- and poly-; most esters, except those of phenolic acids; higher alcohols, ketones, ethers. Also some salts, mainly of stronger acids. *b*. Some of the latter may be ppd. from aq. soln. by NaOH; also some esters; and alkaloids from their salt solns. XVII.
2. *a*. The mixture, with or without warming, becomes turbid, giving either an emulsion or oily drops, often with characteristic smell.	Salts of aromatic amines or hydrazines give Na salt and free base (smell). VIII, X, XI, XIV, XV. Aromatic aldehydes give corresponding alcohol and salt of acid. Aromatic acylamines generally need formal hydrolysis, VII, A, B, but may behave as amine salts. *In these cases: extract the amine or alcohol with ether, etc.* Chloral and its hydrate give chloroform and formate. Trichloracetic acid and salts give chloroform and carbonate. } Smell the $CHCl_3$.
b. The turbidity is yellow or brown and has a peculiar smell.	Aliphatic aldehydes, except H_2CO, give this "aldehyde resin." Their cpds. with NH_3 or with $NaHSO_3$ give "resin" and NH_3 or Na_2SO_3 in addition. Aldehyde sugars give a red or brown colour only. XIII.

3. The warm liquid remains clear (nearly), giving off volatile products.	Ammonium salts give off NH_3; so also may amides and nitriles, but these latter generally need a formal hydrolysis. VII, A, B. Salts of aliphatic amines give free base, volatile enough to distil over, often smelling like NH_3 but inflammable. XIV, XV. Ketone bisulphite cpds. give off ketone, generally volatile., XIII, B.
4. The subst. dissolves with change of colour.	Nitrophenols, o-, yellow to red; p-, colourless to yellow. IX, A. Also other coloured pseudo-acids.
5. The subst. dissolves more or less quietly, without further visible change.	Carboxy acids and anhydrides; sulphonic acids; the acid halides of both (vigorously); quasi-acids, *e.g.* ring HO cpds. simple or substituted, as phenols, chlorophenols, naphthols, also aliphatic nitro cpds. Also a number of other cpds. very sol. in water.

β. Shake up the mixture with free access of air, warming.

6. Brown to red or black colours are developed by air oxidation.	Polyhydroxy cpds. (ring) and some of their derivatives; catechol, at first green, then brown to black; resorcinol, brown; pyrogallol, brown to black; quinol, first green (quinhydrone), then yellow (quinone). XI.

γ. Put 2-3 c.c. N/10 NaOH into a t.t. Just colour it with phenolphthalein. Add some O.S. Cork up and shake well.

7. *a.* The colour remains:	Subst. cannot be an acid of any kind.
b. The colour is discharged.	Subst. belongs to the classes—acid, quasi-acid (above), acid salt; or an easily hydrolysed derivative of these as halide, anhydride, or ester (oxalate, salicylate); salt of amine.

VII. HYDROLYSIS.

A. Hydrolysis by Alkali.

This reaction is necessary for the identification of so many substs. that it should be begun early and allowed to go on while applying other tests. Some reactions already given V, VI, will be observed here also. They will not again be described.

Fit a small round-bottomed flask to some form of reflux water condenser. Mix 50 c.c. of aq. NaOH, with about 10 gm. of the subst. in the flask. Boil with pieces of porous pot, on a sand bath, until by disappearance of smell or of unmixed layer, the reaction appears complete, or, in general, for as long a time as can be given to the operation. Some substs. may require alcoholic alkali, *e.g.* **ethyl-alcoholic KOH, but this introduces obvious difficulties, in identification of alcohols.** See *post.*

The operation might be carried out thus:—Mix as above in a stoppered bottle, about one-third full. Tie down the stopper. Suspend it in a water bath and heat gradually to boiling. Keep it so for a short time. Let cool completely, and cautiously open the bottle. Filter off any solid residue, or separate any unmixed layer by a tap funnel.

This may include unhydrolysed cpd. or insol. hydrolysis product.

Fit up the condenser for distilling off any volatile part. Distil off on a sand bath.

The effect, essentially that of addition of water, in the form H, OH, results in decomposition into (*a*) a basic part, alcohol, amine, etc., in the distillate unless too nonvolatile; and (*b*) an acid part, organic or inorganic, remaining behind in union with the alkali.

Add to the distillate, solid NaCl or $CaCl_2$. Separate any layer by a tap funnel.

This "salting out" removes any unhydrolysed ester, higher alcohols, ketones, etc.

Test this, and the distillate, by Oxidation VIII **and** X A, **after drying by CaO. Extract the amines, less volatile, from the alkaline residue by ether, shaking up well. Separate by tap funnel. Dry the soln. by KOH sticks broken to the size of rice. Evaporate off the ether on the water bath.** Apply tests X B, XV, VIII, XI.

From the residue, from which any ether should have been evaporated, the organic acids may be obtained in the free condition as follows:—

a. **if insol. in water by acidifying with dil. H_2SO_4 and filtering off.**

b. **if volatile, by distilling the residue, after evaporation, with conc. H_2SO_4.**

c. **if sol. in water and nonvolatile, by acidifying with dil. H_2SO_4 and extracting with ether or other immiscible solvent. Or use method of X, XII, XI.**

1. All hydrocarbons, alcohols, amines, ethers, ketones, aromatic ring halogen and nitro cpds., isocyanides, many carboxy- and sulphono-salts, salts of quasi-acids remain unaffected. Of these, lower alcohols and many salts dissolve merely.

2. Unsubstituted carboxy and sulphonic acids, aliphatic nitro-cpds., phenoloid cpds. simple or substituted, anhydrides of carboxy acids, dissolve, forming sol. salts. See XI, XII.

3. *a.* Aliphatic halogen cpds., mono-, di-, etc., give corresponding HO-cpd., mono-, di-, etc. These may be alcohols, mono-, di-, etc., primary, secondary, tertiary; aldehyde or ketone hydrates, unstable and eliminating water. VIII A, X A. XIII.

Chloroform and carbon tetrachloride give formate and carbonate respectively; chloral, etc., give chloroform (above) and formate. IX A, VIII C, XIII.

b. Halo-substituted aliphatic acids give hydroxy acids, these being either alcohol acids (monochloracetic gives glycollic), aldehyde acids (dichloracetic gives glyoxylic), or ketonic acids; but trichloracetic gives at first carbonate and chloroform (above): with, of course, sodium halogenide, in each case. IX A.

4. Ordinary organic esters and organic and inorganic ester-acids and their salts, *e.g.* alkylsulphates, give alcohol, etc., as above; and salts of acids, organic or inorganic. Alcohol, VIII, X A., Acid, XII, XI, X.

5. Aromatic aldehydes give salt of corresponding acid and corresponding alcohol, but aliphatic aldehydes give "resins." See VI. *b*. Aldehyde acids behave similarly to the former, thus glyoxylic acid gives glycollic and oxalic acids.

6. Ketonic acids, their salts and esters, give ketones, carbonate and alcohol: also, they can give salts of two acids, and alcohol, this being the main reaction when conc. alcoholic KOH, is used. XIII.

7. Acid amides and nitriles (alkyl, etc. cyanides) evolve ammonia, leaving salt of acid (acetamide and methyl cyanide both give ammonia and acetate). XI.

Alkaline cyanides, after long boiling, give formate and ammonia. XII.

Amic acids, *e.g.* oxamic, and esters, give organic salt, ammonia and alcohols.

8. Urethanes, *i.e.* carbamic esters, give carbonate, ammonia, and alcohols. Other amino-acids, *e.g.* aminoacetic, are not decomposed in this manner. IV.

9. Acylamines, acylhydrazides, give amine, hydrazine, more or less volatile, and salt of carboxy-acid. Aliphatic amines, being volatile, distil over like alcohols, the less volatile aryl-amines and -hydrazines may be extracted by ether, as described above, or as follows:—

Fit up an oilcan as boiler, pass steam from this into the alkaline liquid in a flask heated on a sandbath and connected with a condenser. The amine, etc., distils over with the steam. In this liquid it can be identified by the tests XIV., XV., or, extract with ether, etc., as above, p. 184.

10. Sulphonic esters, chlorides, amides, give sulphonates, and alcohols, chlorides, or ammonia respectively. XVI.

11. Phenol esters give phenate, and salt of the acid. XI, XII.

Separate as given under Phenol Esters and identify each by proper tests.

With alcoholic KOH, the method is similar to that above, using the same quantities. The results in general are similar to those above, but the distillate will include EtOH and salts of various acids may be ppd. by the alcohol, chlorides, sulphates, oxalates, etc. Also halogen cpds. give unsaturated cpd. by elimination of HX as also may some other series of cpds.

The unsaturated cpd. may be either ethylenic—Apply Tests VIII B, XI, XIX.—or acetylenic Apply Tests VIII B, XI, XIX.

B. **Hydrolysis by Acids.**

In this case the acid part is set free, while the other part, if sufficiently basic, remains combined with the acid used, generally dil. sulphuric.

Repeat the previous operation, using 50 c.c. of dil. H_2SO_4 to 10 gm. of subst.

On distilling, volatile acids pass over; non-volatile ones can be extracted by the appropriate immiscible solvent, or by a pptn. method. See XII, XI. Alcohols also distil over, as they would not react with the dil. acid. Bases, remaining as sulphates, can generally be identified directly in that form by the proper test, XIV, XV, XVII. Or apply then method of VII.

The results repeat and supplement those of the last operation, and so only characteristic cases are here mentioned.

1. Ethers, after long boiling, give alcohols, two molecules, the same or different (when the ether is a "mixed" ether). VIII, IX A.

2. Alkylates, phenates, give sulphate and free alcohol or phenol. VIII, XI.

3. Ketonic acid esters give ketones, CO_2, and alcohol. XIII, VIII.

4. Amides, nitriles, metallic cyanides, urethanes, and other cpds. evolving ammonia with alkali leave, of course, NH_4 salt, and give free acid. XI, XII.

5. Similarly also, cpds. which would leave carbonate with alkali, evolve carbon dioxide in this case, *e.g.* urea, urethanes, cyanates (+ HOCN, some).

6. Acylamines and acylhydrazides give free acid, XII, and salt of base. XIV, XV.

7. Hydrazones and oximes give free aldehyde or ketone, and salt of the base. XIII.

8. Aldehyde and ketone addition cpds., such as aldehyde ammonias, aldehyde and ketone bisulphite cpds. separate into their generators. XIII.

9. Glucosides give a sugar, often glucose, and some HO-cpd., often aromatic, which may decompose further; thus amygdalin gives mandelonitrile and maltose, the former going into benzaldehyde and HCN, the latter into glucose, two molecules.

Sucrose gives glucose and fructose. VIII C., XI.
Starch gives dextrin, maltose, and finally glucose. VIII C, VI.
Cellulose, after long boiling with stronger acid, gives glucose. VIII, VI.

VIII. THE OXIDATION REACTION.

A. Oxidation with Dichromate and Dil. Sulphuric Acid.

Mix subst. with plenty of dil. sulphuric, gradually add potassium dichromate powder, warming gently, in a large t.t. or small flask. Note result at intervals. Collect any volatile products by passing them, by means of a fitted delivery tube, into a little water in a t.t. standing in cold water.

If the red colour changes to green, there is evidence of oxidation, but the products may not be identifiable, as being either difficult to separate or not characteristic enough in themselves.

1. *a*. Primary alcohols give aldehydes, then one acid of same carbon content. XII.

   b. Secondary alcohols give ketones, then two or more acids. See XIII., XI., XII.

   The aldehydes and ketones may be distilled off and identified.

   c. Tertiary alcohols give ketones first, then various acids. See as above.

   d. Aliphatic ethers, amines, halogen and other esters, give results suggesting that hydrolysis into alcohol had happened first.

   e. CCl_4 is unoxidisable; chloroform gives carbonyl chloride, $COCl_2$.

   This may be identified by its smell, and reactions of an acid chloride. V.

2. *a*. Aldehydes give one acid of same number of carbon atoms. XI., XII.

   b. Ketones give two or three acids. XI., XII.

These operations generally require long boiling under reflux condenser, distilling off the acids, if volatile, or extracting them with ether if not. But the operation may be carried out in a stoppered bottle as already described.

3. *a*. Aliphatic acids, simple, are in general unchanged, as also benzoic, phthalic.

   b. Hydroxy acids, being alcohols as well, are oxidised to aldehyde- or to keto-acids or further to dicarboxy acids. See ketones above.

   c. Halo-acids may behave like haloid esters (*q.v.*) 1 *d*., also VII. 3. *b*, IX. A. *a*.

   d. The side-chains of aromatic acids are oxidised into COOH. See B. 2.

4. *a.* Primary aromatic amines, even if substituted, and their salts, give various coloured substs. and finally a quinone, except p-toluidine. XIV., XV.

   The quinones are volatile solids, of yellow colour and peculiar smell.

   b. Aromatic acylamines may behave similarly by precedent hydrolysis.

   c. Secondary and tertiary aromatic amines give various coloured substances otherwise uncharacteristic. XV.

5. Complex aromatic hydrocarbons, *e.g.* naphthalene, anthracene, phenanthrene, give yellow to red quinones, sublimable, but often odourless.

6. Polyhydroxybenzenes are also oxidised, but the products are uncharacteristic, except that quinol gives benzoquinone. See 4. *a.*, C. 5, D. 2.

7. Aliphatic hydrocarbons and benzene are oxidised with extreme difficulty and, if at all, generally completely, *i.e.* to CO_2 and water.

B. **Oxidation with Alkaline Permanganate.**

Mix the subst. with conc. $KMnO_4$ soln. and a few drops of alkali. Warm, gently at first, in a t.t. with delivery tube; (or use the stoppered bottle as described above). After the oxidation, either filter the liquid, washing the muddy residue on the filter, and acidify the filtrate with dil. sulphuric; or pass SO_2 into the mixture, or add sulphurous acid, without filtration.

The $KMnO_4$ soln. should become distinctly turbid, otherwise the test gives no definite evidence. The acidification pps. insol. acids, mostly aromatic, and the SO_2 converts the "manganese mud" into $MnSO_4$ and also pps. the acids.

The results in general repeat those with $K_2Cr_2O_7$, for which reason the distilling off of volatile products may here be omitted, but characteristic cases are here mentioned.

1. Unsaturated cpds. are oxidised, often with production of dihydroxy cpds., which in some cases are uncharacteristic —allyl alcohol gives glycerol, cinnamic acid a dihydroxy acid; in other cases with rupture at the double bond, producing aldehydes which then pass further into acids. XIII.

2. Aromatic cpds. with alkyl side-chains have these oxidised completely, *i.e.* into COOH, so that some acid, substituted or not, is the product. Toluene and ethylbenzene both give benzoic; the xylenes give the phthalic acids; naphthalene gives ortho-phthalic. Nitro-, chlor.-, etc., toluenes give nitro-, chlor.-, etc., benzoic acids, which are ppd., but the monohydroxy toluenes, *i.e.* the cresols, are not oxidised.

   This is the method of proving the presence of alkyl side-chains in aromatic cpds., *i.e.* of distinguishing between substituted toluenes or xylenes, and similarly substituted benzenes, which are not oxidised by this reagent.

C. **Oxidation with Fehling's Soln.**

Neutralise the subst. with NaOH, add the reagent, and warm to boiling, in a t.t. with delivery tube. Distil over, and collect any volatile products as usual.

A red pp. of cuprous oxide shows oxidation.

1. Aldehydes, aliphatic only, and aldehyde and ketone sugars, give acid, simple in former, complex in latter case. See XI., XII., VI.

2. Sucrose, and glucosides, do reduce, after Hydrolysis (*q.v.*) VII. B.

3. Hydrazines give the corresponding hydrocarbon, and nitrogen; thus phenyl hydrazine gives benzene, to be distilled over and identified. See XVIII.

4. Formic acid and formates, and chloroform are also oxidised, to CO_2, etc.

5. Of the polyhydroxybenzenes, catechol, quinol, and pyrogallol also reduce.

D. **Oxidation with Tollens' Reagent: Ammoniacal Silver Nitrate.**

Mix the subst. with the reagent in a very clean t.t. Warm this in a water bath.

Metallic silver is produced, and may form a mirror on the inside of tube.

1. Aldehydes, aliphatic and aromatic, also aldehyde and ketone sugars.
2. Polyhydroxybenzenes, catechol, resorcinol, quinol, pyrogallol, even in cold.
3. Tartaric and salts also reduce; citric and salts give only a black pp.
4. A white pp. here, of Ag substitution derivative is the characteristic reaction for acetylenic unsymmetrical cpds., *i.e.* those containing the group ·C⋮CH. See XIX δ.

IX. REDUCTION.

A. **Incomplete Reduction.**

a. For Halogens.

Mix the subst. with abs. alcohol and add pieces of sodium as long as they dissolve rapidly. When the last piece of Na has gone, add water, divide into parts.

a. **Add dil. H_2SO_4, $FeSO_4$Aq. and $CuSO_4$, Aq.**

A whitish pp. of cuprous iodide proves the presence of iodine.

b. **Acidify with dil. HNO_3 and add $AgNO_3$, Aq.**

A white pp. of AgCl proves the presence of chlorine;

a yellowish pp. of AgBr proves the presence of bromine;

a yellow pp. of AgI proves the presence of iodine.

For complete distinction, use ordinary inorganic methods, applied to this same solution evaporated to dryness.

β. For Nitro, Nitroso, Azo, cpds.

Mix the subst. with conc. HCl, heating on a water bath. Add $SnCl_2$ cryst., little by little. Boil for a short time. Use a t.t. or small flask with air condenser.

The disappearance of colour and smell indicates the end of the reaction.

Divide the mixture into three parts.

a. **Dilute to some extent, pass in H_2S.**

A yellow pp. of SnS_2 proves the oxidation of the $SnCl_2$; a chocolate one of SnS shows nitro group absent or that too much $SnCl_2$ had been used.

b. **Add more O.S. to a second part and repeat boiling, and testing.**

c. **Add excess of NaOH, Aq. to another part, then test for primary amine by XIV, XV.**

If amine is found, and (a) succeeds, then nitro- (etc.) group is present. Distinguish further by smell, etc.

B. **Complete Reduction: Hot Zinc Dust.**

This removes oxygen, sulphur, the halogens, etc., sometimes even adding hydrogen, so that most substs. are brought down to the corresponding saturated hydrocarbon; nitrogen is often eliminated as ammonia NH_3.

Mix with excess of zinc dust as directed for soda lime and heat as there described. Collect any volatile products. Omit this if NO_2 group present.

1. Saturated hydrocarbons, including benzene, naphthalene, of course are not changed, nor are certain stable N-ring cpds., like pyridine.
2. Unsaturated hydrocarbons may be partly reduced to saturated hydrocarbon, or partly evolved as such.
3. Most saturated aliphatic cpds. give corresponding saturated hydrocarbon, *e.g.* alcohols and their esters, ketones, aldehydes.

4. Halogen cpds. may sometimes lose only the halogen, the residues uniting. Thus brombenzene should give diphenyl.

5. Aromatic ring cpds., especially hydroxy cpds.—phenols and naphthols—give corresponding hydrocarbon.

X. A. ESTERIFICATION: FOR ALCOHOLS.

The alcohol is made into an ester of characteristic smell.

Apply to O.S., or to a dehydrated alcohol from hydrolysis. Mix with the appropriate acid (below) or its anhydrous Na salt. Add a little conc. sulphuric and warm gently. Note any characteristic smell then, or after pouring into water.

Characteristic results are: Methyl, Salicylate; Ethyl, Benzoate; and Ethyl, Propyl, Amyl, Acetates.

Or, use some form of the Schotten-Baumann method:—Mix with acetic anhydride. Warm gently, pour into water or a dil. soln. of Na_2CO_3. Note smell.

Or, mix with acid chloride, acetyl or benzoyl, warm, and pour into water: or, with benzoyl chloride, add this and NaOH dil. alternately, in small quantities.

This test may also be used, conversely, as a confirmation for certain acids.

Apply to O.S. or dry acid or salt from hydrolysis. Add the appropriate alcohol and a little conc. H_2SO_4.

Acetic, with amyl alc.; Salicylic, with methyl alc.; Benzoic, with ethyl alc.; Cinnamic, Phthalic, Succinic, etc., with ethyl alc.

X. B. ACYLATION: FOR AMINES.

Amines, other than tertiary, will in general form acyl derivs., which, especially in the case of arylamines, crystallise readily.

Apply to O.S., or to a dehydrated amine from hydrolysis. Mix with acid anhydride, acetic generally, in t.t. Warm for a time on sand bath. Pour out into a little cold water or dil. Na_2CO_3. Filter off the solid. Recrystallise from the minimum quantity of boiling water. Dry completely and take m.p.

XI. REACTION WITH FERRIC CHLORIDE.

This reagent acts in various ways :—

1. Gives colour reactions, not always of known nature.
2. Gives pps. of salts, etc., with certain acids, etc., often of basic salt.
3. Acts as an oxidising agent, as possibly also in some of above cases (1).

Take soln. of O.S. (in alcohol if necessary), residue from alkaline hydrolysis made neutral with dil. HCl, distillate or extract from acid hydrolysis made neutral with caustic soda. Add ferric chloride. Note result. Then add dil. HCl.

1. A colour reaction is obtained.

i. The colour disappears :—	*a*. Violet, from phenol, salicylates, phenolsulphonates.
	b. Blue, from cresols, morphine.
	c. Green, from guaiacol, catechol ; **add $NaHCO_3$ to same part** violet red in latter case.
	d. Dark violet, from resorcinol.
	e. Reddish brown, from pyrogallol.
	f. Violet red, from esters of keto-acids like acetoacetic.
	g. Red, from acetates, formates. See below, 2. γ. *b*.
ii. The colour remains :—	*a*. Deep red, opaque, from thiocyanates.
	b. Greenish brown, from ferricyanides.

2. A pp. is obtained.

i. The pp. is not changed by HCl.	Deep blue, from ferrocyanides.
ii. The pp. changes into one of acid, or quasi-acid, white crystalline.	*a.* Buff, of basic benzoate; gives crystalline flakes of acid. *b.* Light yellow, of basic cinnamate; gives crystalline flakes of acid. *c.* Brownish-pink, of hippurate; gives crystalline pp. of acid. *d.* Reddish brown, of phthalate; acid ppd. only in conc. solns. *e.* Violet flakes, from α-naphthol. *f.* Green pp. from β-naphthol.
iii. The pp. dissolves :—	*a.* Light brown, of basic succinate. So also phthalate possibly. *b.* Brownish, of basic acetate or formate; ppd. only on boiling.

3. The subst. is oxidised into different cpds., of characteristic properties.

a. Aromatic primary amines give various coloured products.

b. Quinol gives green needles of quinhydrone.

c. Paraminophenol gives the violet colour from phenol.

d. Phenylene diamines give a red colour.

On warming, these, except p-toluidine and o- and m-phenylene diamine, pass into (yellow) quinones (smell).

e. Alkyl and aryl mono-hydrazines give nitrogen and hydrocarbon. The aromatic hydrocarbons formed here may be distilled off and identified as given under phenyl hydrazine. XVIII.

XII. TEST FOR ACIDS: BY PRECIPITATIONS.

Acidify O.S. or part of residue from either acid or alkaline hydrolysis, with HCl, add $BaCl_2$.

1. White pp. Sulphate: from sulphates or alkylsulphates.

Acidify the above with HNO_3, add $AgNO_3$.

2. White to yellow pps. Halogen Acids: from Halogen Salts or Haloid Esters.

   Apply inorganic methods for distinction.

Acidify another part of above with HOAc, add $CaSO_4$.

3. White pp. Oxalate: from salts and esters.

Test another part of above with $FeSO_4$ and conc. H_2SO_4.

4. Brown ring. Nitrate: from salts and esters.

   Nitrites: give a brown colour with $FeSO_4$ and dil. H_2SO_4.

Neutralise another part of above as for XI. Add $CaCl_2$, warm mixture, let stand.

5. White pp., soon, tartrate.
6. White pp., on long boiling, citrate.

Neutralise another part as above. Add $BaCl_2$ and alcohol.

7. White pps. Succinate. Phthalate.

XIII. A. THE ALDEHYDE REACTION: SCHIFF'S TEST.

This is a very general reaction for the less complex aldehydes. It is due to the formation of certain condensation products, not to the restoration of the original (magenta) colour.

Mix O.S., dichromate or permanganate oxidation product, or distillate from acid hydrolysis, with Schiff's R., cold, shaking well in closed t.t. Let stand.

A red to purple or violet colour appears, varying in tint and time.

Formaldehyde and acrolein give nearly violet colour.

Benzaldehyde and salicylaldehyde give this reaction, but slowly.

XIII. B. COLOUR REACTION FOR SOME KETONES.

Mix a few drops of a fresh made soln. of sodium nitroprusside with a little of the ketone, add a few drops of ammonia, cold.

A violet or violet-red coloration is produced, disappearing on warming but reappearing on cooling.

Acetone and acetophenone give this test, the latter slowly.

XIV. THE ISOCYANIDE REACTION.

The type reaction for cpds. containing the primary amino-group NH_2, sometimes obtainable even when the cpd. is substituted in the chain or ring.

Mix O.S., distillate or extract from alkaline hydrolysis, or distillate from soda lime fusion, with excess of aq. NaOH or of alc. KOH, add one or two drops of chloroform, and warm.

The disgusting smell of isocyanide, alkyl or aryl, is produced, from primary amines, or from their acyl derivatives hydrolysed by the alkali; also from primary diamines, but the smell in these cases, and in those of chain or ring substituted amines, may not be exactly the normal one of a simple isocyanide.

XV. REACTION WITH NITROUS ACID.

This reaction takes various forms, according to the case in point. All are condensations, however, water being eliminated.

A. **Dissolve O.S., or extract from alk. hydrolysis in excess of dil. H_2SO_4. Add, drop by drop, soln. of sodium or potassium nitrite, cooling well, until a drop gives a blue spot on starch-KI paper,** *i.e.* **excess of nitrite is present.**

1. A brown or reddish pp. is formed.

(*a*) **Add excess of NaOH, Aq.**

This passes into a green flaky pp.

Tertiary aromatic amines give p-nitroso-cpd., salt passing into base.

2. A brown colour or pp. is produced: unchanged with alkali. Metaphenylene-diamine gives "Bismarck Brown."

3. A yellow oil or solid is formed, of peculiar odour.

   (β) **Extract with ether; apply Liebermann's Test to ether extract, after evaporation.**

   Secondary amines, aliphatic and aromatic, give nitrosamines.

4. The liquid becomes yellowish and of peculiar odour: due to diazo cpd.

   (γ) **Keep well cooled: to a part add β-naphthol in NaOH.**

   Immediate scarlet pp. or colour of a dyestuff.

   (δ) **Boil the other part. Identify the product by phenol reactions XI.**

   Primary aromatic amines give diazo cpd. forming in (γ) a dyestuff, in (δ) a phenol.

5. The liquid evolves nitrogen . no other visible reaction.

   (ϵ) **Fit a delivery tube: distil over. Identify the alcohol.**

   Aliphatic primary amines pass directly into alcohol corresponding and N_2.

6. The liquid undergoes no identifiable change.

   Aliphatic tertiary amines give no reaction.

B. Use O.S., extract from alk. hydrolysis, after acidification or passage of CO_2, or extract from acid hydrolysis. Add conc. H_2SO_4 containing a small quantity of nitrous acid, *i.e.* $NaNO_2$. (α) **Then dilute with water.** (β) **Then make alkaline.**

7. Phenoloid cpds. give a red colour: (α) passing into green; (β) then into blue.

   Apply this test, Liebermann's, thus to nitrosamines. Mix with an excess of phenol dissolved in conc. H_2SO_4. Then dilute, and make alkaline, as above.

   The same sequence of colour reactions is observed.

XVI. POTASH FUSION FOR SULPHONATES.

This is the form necessarily taken by hydrolysis in the case of the very stable sulphonic cpds., converting them into sulphite and hydroxy cpd., alcohol if aliphatic, phenol if aromatic; the latter remaining combined with the KOH, the former being volatilised.

Make a little tray 5 × 3 × 1 cm. by pinching up the corners of a piece of copper foil. Fuse in this a few pieces of KOH. When in quiet fusion, add the subst. Continue heating until in quiet fusion without much darkening in colour. Let cool partly, and drop into a beaker of cold water. Acidify with dil. sulphuric.

The mixture evolves SO_2 indicating a sulphonic cpd. (or a bisulphite cpd., see VI., XIII.).

Warm, to drive off most of the sulphur dioxide.

Then the smell of phenoloid cpd. becomes apparent. This may be phenol or the cresols, from benzene- and the toluene-monosulphonates ; and α- or β-naphthols from α- and β-naphthalene-sulphonates.

Neutralise and filter the soln. Test with ferric chloride. Or; extract the acid liquid with ether. Separate. Drive off the ether on the water bath. Test with $FeCl_3$ XI.

This latter method makes the recognition of the above more certain and also allows of the detection of resorcinol and other dihydroxy cpds. which are odourless, these indicating disulphonates or phenolsulphonates.

Alkylsulphonates are rather uncommon substances.

Substituted aryl-sulphonates may give substituted phenols, *e.g.* nitro-arylsulphonates, but if the substituent be a halogen, that is replaced by OH as well, di-OH cpds. resulting.

Sulphonamides and sulphonic chlorides give in addition: ammonia, volatilised in the fusion, and chloride, original in the residue, respectively.

By an exception, arylamine sulphonic acids, *e.g.* sulphanilic, naphthionic, give arylamine, volatilised in the fusion of course, and sulphate, not aminophenol, etc., and sulphite.

XVII. REACTION FOR ALKALOIDS.

This depends on the formation of certain insol. salts, etc.

Dissolve O.S. in water or dil. acid.

α. **Add phosphomolybdic acid.**

Most alkaloids give yellow pps. of phosphomolybdate.

β. **Add potassium mercuriodide.**

Most alkaloids give yellowish pps. of mercuriodide.

γ. **Add Iodine in KI, Aq.**

Many alkaloids give brown pps. of per-iodide.

See these for confirming tests.

XVIII. TEST WITH NITRIC ACID: NITRATION.

The results obtained in this test with aliphatic cpds. are mainly Oxidations, more or less violent. It is most characteristic as a reaction for aromatic cpds., and is specially intended for the hydrocarbons among these.

α. **Mix the subst., cautiously, with conc. nitric acid in a t.t., warming gently.**

1. A violent reaction sets in, with much evolution of nitroxides (brown). Many aliphatic cpds. are oxidised, alcohols, ethers, aldehydes, ketones violently, mostly into acids, often oxalic, as in the case of the sugars.

β. **If reaction is not violent, mix in t.t. with a little conc. sulphuric and conc. nitric. Warm gently in a water bath, shaking well. Pour into cold water. Blow out any brown fumes of nitroxides. Note any characteristic smell.**

2. Most aromatic cpds. are nitrated; some are also oxidised as well, and with the production of so much tarry matter that no recognisable products can be isolated, *e.g.* amines, hydrazines, polyhydroxy cpds.

3. Aromatic hydrocarbons, their haloid and nitro-derivatives, the latter with some difficulty without fuming nitric, give recognisable products. The mono-nitro-cpds. from the hydrocarbons, have generally a characteristic smell and are insol. in water and aq. solns.

   Apply to the product, in any case, Reaction IX A. b. confirming as there given.

4. Aromatic mono-HO-cpds., *i.e.* phenoloid bodies, give nitro-derivatives, of which the mono-nitro-cpds. often have characteristic smell and colour, and are sol. in water and in alkalis, being quasi-acids. Some tar is formed.

5. Aromatic carboxy and sulphono-acids and their derivatives are also nitrated, but the products are less specifically characteristic than the originals.

6. Phenol ethers behave much as the hydrocarbons do.

   Apply to the product Reaction IX A. b. to prove the presence of the NO_2 group in the above cases, after pouring into water (or distilling in steam as VII. A. 9).

XIX. REACTION FOR UNSATURATION; ETC.

Addition of halogen (Br_2 here) proves unsaturation, but some substitution reactions are sufficiently characteristic to be useful as tests.

a. **Dissolve a little O.S. in CCl_4 in t.t. Add Br_2 in CCl_4. Warm on the water bath or heat mixture in a stoppered bottle as already described.**

a. The colour of the Br. disappears without other visible change.

   The substance is most probably unsaturated.

b. Colourless fumes of HBr are evolved.

   This is bromination, *i.e.* substitution.

β. **Add some Al/Hg. couple or a few iron nails and warm as before.**

c. The Br colour goes, HBr fumes being evolved.

Most substs. containing H attached to C react by substitution. This is almost the only positive test for aliphatic saturated hydrocarbons. It is given also by aromatic hydrocarbons.

γ. **Dissolve some O.S. or hydrolysis extract in water; add Br, Aq.**

d. A bromo cpd. is formed and often ppd., HBr remaining dissolved. Phenoloid cpds. and their derivatives, *e.g.* salicylic acid, cresols and resorcinol give pps. white or yellowish white, consisting of the tribromo-cpd. in these cases mentioned by name. Aniline and some of its derivatives and homologues also give pps., tribromo- in the case of aniline.

e. The bromine colour goes but without other striking change. Many cpds., especially aliphatic, are oxidised in this way, some brominated as well, *e.g.* alcohols give bromaldehydes, aldehyde sugars give the corresponding acid.

δ. **Add ammoniacal cuprous chloride to the subst.**

True acetylenic cpds., *i.e.* those containing ·C : CH give a red, brown or yellow pp.

XX. A CONFESSION OF FAILURE.

If the preceding tests have been worked through without obtaining any clues, then determine the elements present as in Chap. I. Elementary Composition and work over the Tests again with this knowledge as a guide.

SECTION 2. ANALYSIS OF MIXTURES.

The complexity of the reactions of organic cpds., is such that the analysis of any mixture, within a given time, may be an impossibility. Cases such as the working up of crude products like coal tar, bone oil, or raw materials of plant or animal origin, or of the "messes" which often are the results of synthetical reactions, or which occur in the determination of the structure of a complex body like an alkaloid, are obviously lengthy.

But mixtures of reasonable simplicity may be analysed as completely if not as expeditiously as inorganic mixtures.

As in the latter case, separation of the constituents is generally necessary, though the constituents being compounds and not ions, the separation methods are not so simple nor so expeditious.

In some cases, however, the class or group to which one or more constituents belong may be more or less definitely determined without a separation, and any evidence of value which can be obtained on this point by application of Tests in the ordinary Scheme given at the commencement of this chapter is useful in suggesting which separation method is likely to be most effective. But as the physical properties have to be relied on for a complete identification, a separation into pure constituents is necessary.

That being so, apply to parts of the mixture the following tests of the Scheme, noting in particular the points mentioned.

I. Physical state, smell, taste, etc.

II. Ignition in the open and in the closed tube.
Nature of flame, smell of vapours.

III. Action of conc. Sulphuric Acid.

XI. Action of Ferric Chloride.

XII. The pptn. of insol. salts either from free acid (neutralised first) or from sol. salts present.

XIII. Reaction for Aldehydes and Ketones.

XIV. Isocyanide Reaction.

XV. Reaction with Nitrous Acid.

The last five tests may be depended on to give fairly definite evidence for the groups to which they apply, even in presence of some cpds. belonging to other groups, but not, of course, if more than one cpd. reacting with the reagent be present.

Separations may be made by the following methods:—

Fractional distillation, including distillation in steam.

Fractional solution, by different solvents.

Elimination of a constituent in soln. by changing the nature of solvent by an addition to the latter, as in "Salting Out."

Fractional Crystallisation.

a. **Fractional Distillation.**

This is the best method for liquids in mixture, or for solutions of solids in liquids. It should be begun as early as possible.

Fit up a fractionation apparatus—a distilling flask with thermometer connected with a condenser and receiver—and distil the mixture, first over a water bath then over sand or oil. Note the thermometer reading. If this rises steadily, change the receiver at any convenient temperature, thus a fraction 60° to 80° will contain some important possible constituents, one from 85° to 95° would be largely free from ethyl alcohol, benzene, etc., while higher homologues of these would be still to come. So also a fraction 170° to 185° would contain a number of important substs. and 185° to 200° another series. See Scale of M.P.'s and B.P.'s.

But if temperature remains steady for a time, wait until it does rise, collecting all that will come off together at the same temperature.

This will be either one constituent, or a constant boiling mixture of them.

In the previous case the fractions may each be redistilled, using a fractionating column if the fractions are within close limits.

When samples boiling at fairly definite b.ps. have been obtained, apply to them the tests of Scheme, with the clues given by boiling points.

Often a Steam Distillation is an effective method of separation.

Fit a flask or oilcan as boiler with a long safety tube, and a delivery tube passing to the bottom of a flask containing the mixture and lying in an inclined position. This is connected with a condenser and receiver. When "steam is up" let it pass through the mixture, also heated. Collect the distillate, separate in tap funnel, or extract with ether as below, Section II. Apply to it tests of Scheme.

β. Fractional Solution.

The most useful method for solids, sometimes applied to liquids: separation by dissolving out different constituents by different solvents, physical or chemical, not common to both. Useful solvents are :—

Solvents	
a. Water. *b.* Ethyl Alcohol.	Common to many solutes, acids and their salts.
c. Ethyl Ether. *d.* Chloroform. *e.* Benzene.	For substs. insol. in water, *e.g.* substs. not salts.

A separation by using one of these solvents may not be complete, obviously. Therefore it is better to use two solvents, one from each class above, *i.e.* to extract all water-soluble constituents from one sample, and all ether-soluble or chloroform-soluble constituents from another, to avoid the trouble of drying.

Shake up the mixture with water in a small flask warming gently (don't boil) as long as anything appears to dissolve. Filter off any solid residue, or if liquid separate in funnel. Use undissolved part for tests in Scheme.

Apply to part of aq. solution tests in Section IV. of Scheme for acidity. Evaporate the rest either to crystallisation or to dryness on the water bath. Apply Scheme Tests to residue.

Shake up another sample with ether or $CHCl_3$ in a closed flask. Filter off residue, dry it, and apply Scheme Tests to it.

Distil off ether, etc., from the solution, fractionating if a liquid. Then use it for tests of Scheme.

Fractional Solution by Differences of Function.—Apply the method used in working up Coal Tar products, extracting bases with acid, acids with alkali.

Shake up mixture with dilute H_2SO_4 (or conc. HCl, for weak bases like Ph_2NH). Filter or separate in funnel. Dry residue; apply Scheme Tests to it.

To solution add dil. NaOH to set free bases. Filter off solid, separate liquid in funnel, or extract with ether. Dry soln. with KOH or K_2CO_3.

Shake up another sample with dil. NaOH. Separate as above. Residue may be used for Hydrolysis, VII. in Scheme.

Liberate acids by dil. H_2SO_4. Filter or extract with ether. Dry solution with $CaCl_2$ or Plaster of Paris.

Distil off ether from solution of bases and of acids, finishing by fractionation, or by Steam Distillation especially for solids. Apply Scheme to these.

"Salting Out" and **similar methods.**

Of the organic substs. soluble in water many do not dissolve in aq. solutions. Thus purely basic cpds. are generally insoluble in alkali solutions, purely acid cpds. insoluble in dilute mineral acids. But cpds. of double function may dissolve both in acid and in alkali solutions, *e.g.* aminophenol in alkali, because phenolic, and in acids as an amine.

Of other water-soluble substs. many are insoluble in NaCl, Aq. or $CaCl_2$, Aq. The separation of these from cpds. soluble both in water and in aq. solutions may be accomplished thus,

If all dissolves on making an aq. solution as above, add to the aq. solution excess of solid NaCl or $CaCl_2$ 6 aq. Remove any separated liquid as usual, purify this by distillation and apply Scheme.

Solids are filtered off, to be dissolved in alcohol or ether, etc., as above. Thus acetone, higher alcohols, and aldehydes, etc., of aliphatic division, and many aromatic cpds. rise as oils. Sulphonate salts are generally ppd. on addition of NaCl to aq. solutions of acid or of salt.

Alcohols, etc., soluble in water and in dilute acids and alkalis, are insoluble in K_2CO_3Aq.

> Add to aq. salt solution (above) excess of dry K_2CO_3. Separate as usual. Fractionate the separated liquid as usual. Apply Scheme.

A similar operation may be applied to non-aqueous solutions, namely, adding, *e.g.* petroleum ether to the solution of the subst., then separating as liquid or as solid. Often it is effective to add warm water to warm alcohol solutions.

Of course the separated subst. is not always pure, separation being incomplete.

Fractional Crystallisation.

This has sometimes to be resorted to when the solubilities of the constituents in most solvents are found to be so near, and the possible solvents so limited in number, that separation by different solvents cannot be used.

> Having made the solution in the available solvent, evaporate down slowly, the less soluble cpd. crystallising out first. Obviously the process can hardly ever be complete unless with repetition, this making it tedious. It may be hastened by "inoculating," *i.e.* adding a crystal of one or other of the expected substances.

Naturally it is most common among cpds. of the same kind, ortho, meta, para ring cpds., α or β naphthyl cpds. and other closely-allied isomers.

PART II.

CHAPTER I.

OXIDATION.

Types of Oxidation.

This may take the following forms :—

1. Addition of oxygen with subsequent and consequent elimination of water.

$$\underset{\text{Prim. alc.}}{RCH_2OH} + O \left[= \underset{\text{Alkylidene glycol.}}{RCH(OH)_2} \right] = \underset{\text{Aldehyde}}{RHCO} + H_2O.$$

$$\underset{\text{Secdy. alc.}}{RR'CHOH} + O \left[= RR'C(OH)_2 \right] = \underset{\text{Ketone}}{RR'CO} + H_2O.$$

A characteristic reaction for each of these classes.

2. Addition of oxygen without elimination of water.

$$\underset{\text{Aldehyde}}{RHCO} + O = \underset{\text{Acid}}{RCOOH}$$

$$\underset{\text{Prim. alc.}}{RCH_2OH} + O_2 \left[= \underset{\text{"Ortho" acid}}{RC(OH)_3} \right] = \underset{\text{Acid}}{RCOOH} + H_2O$$

The second equation shows this case as an extension of the Case 1 above. The polyhydroxy bodies shown may exist in an aq. soln., but the elimination of water when two OH groups are attached to the same carbon atom, as in the above, occurs very frequently.

3. Addition of oxygen with H_2O, *i.e.* of (OH),

$$\underset{\text{Ketone}}{RR'CO} + O + H_2O = \underset{\text{Acid}}{RCOOH} + \underset{\text{Oxidised into its own acid}}{R'OH}.$$

A characteristic reaction for the class.

$$\underset{\text{Terty. alc.}}{RR'R''COH} + O = \underset{\text{Ketone}}{RR'CO} + \underset{\text{Alc.}}{R''OH} \quad \text{each oxidised further in its own way.}$$

$$\underset{\text{Terty. alc.}}{RR'R''COH} + O \longrightarrow \underset{\text{Acid}}{RCOOH} + \underset{\text{Alc.}}{R'OH} + \underset{\text{Alc.}}{R''OH}.$$

Each further oxidised

Final product a mixture of acids, including H_2CO_3, *i.e.* CO_2 and H_2O.

This may happen with unsaturated bodies :—

$$\underset{\text{Unsat. hydrocarbon}}{RCH:CH_2} + O + H_2O \longrightarrow \underset{\text{Alkylene glycol}}{R.CHOH.CH_2OH}.$$

$$\underset{\text{Cinnamic acid}}{PhCH:CH.COOH} \longrightarrow \underset{\text{Phenyl } \alpha\,\beta \text{ di-hydroxy propionic acid}}{PhCHOH.CHOH.COOH}.$$

This may happen also with ring cpds., such as the above (3).

4. Addition of oxygen to unsaturated bodies with disruption at the double (or triple) linkage.

$$\underset{\text{Unsat. hydrocarbon}}{RCH:CH_2} + 3O = \underset{\text{Aldehyde}}{RHCO} + HCOOH.$$

$$\underset{\text{Cinnamic acid}}{Ph.CH:CH.COOH} \longrightarrow \underset{\text{Benzaldehyde}}{PhHCO} + (COOH)_2.$$

```
        CH
       / \\
   H2C    CH          H2C.COOH       COOH
    |     |     -->    |         +   |
   H2C    CH          H2C.COOH       COOH
       \ //
        CH
```

Dihydrobenzene into succinic and oxalic acids.

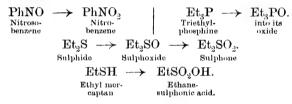
5. Removal of hydrogen as water.

$$C_6H_4(OH)_2 + O = C_6H_4O_2 + H_2O.$$

Hydroquinone — Benzoquinone

$$C_6H_5CH_2CH_2C_6H_5 \longrightarrow C_6H_5CH:CHC_6H_5.$$

Dibenzyl — Stilbene

6. In the above, only C and H are oxidised, but other elements may be oxidised, S as sulphide into sulphoxide and sulphone, also N, P, etc.

Oxidising Agents.

The following are the chief oxidising agents:—

a. **Atmospheric Oxygen, hot,** *i.e.* combustion.

The combustibility of organic substances varies greatly. Some are "spontaneously inflammable," *i.e.* their ignition point is about or below the ordinary temperature, *e.g.* alkylphosphines, zinc alkyls. Others have a very high ignition point, *e.g.* paraffins, the higher fats and oils. Some are almost uninflammable, especially halogen cpds., *e.g.* chloroform, and some are quite so, *e.g.* carbon tetrachloride.

b. **Dichromates of Sodium and of Potassium with dil. Sulphuric Acid,** in various proportions.

An oxidising agent of very general application, but sometimes causing complete combustion.

α. In proportions $3K_2Cr_2O_7$, $1H_2SO_4$, $10H_2O$.

Alcohols give *aldehydes* or *ketones* or *acids*; *aldehydes* or *ketones* give *acids.* Sometimes esters result in part.

Amyl alcohol, $C_5H_{11}OH$, gives amyl valerate, $C_5H_{11}OCOC_4H_9$.

β. In proportions $4K_2Cr_2O_7$ with $6H_2SO_4$, diluted with two volumes of water.

Alkylaromatic hydrocarbons pass into *acids*, the side chain passing into COOH more or less completely; but ortho-disubstituted benzenes, *e.g.* o-xylene, are completely oxidised.

$$\underset{\text{Ethylbenzene}}{C_6H_5CH_2CH_3} \longrightarrow \underset{\text{Phenylacetic acid}}{C_6H_5CH_2COOH} \longrightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH.}$$

γ. In proportions involving much less dichromate.

Aromatic amines (primary) give *quinones*, except p-toluidine.
Aniline, $C_6H_5NH_2$, etc. ⟶ Benzoquinone, $C_6H_4O_2$, etc.

c. Permanganate of Potassium.

α. In alkaline solution.

An oxidising agent of extremely wide application, and seldom causing complete combustion. Mn oxides removed by filtration or by a current of SO_2.

Alkylaromatic hydrocarbons pass into *acids*.
Thus toluene gives benzoic, xylenes give phthalic acids.

Aromatic bodies of form R_2CH_2 pass into form R_2CO.
Diphenylmethane, $(C_6H_5)_2CH_2$, gives benzophenone, $(C_6H_5)_2CO$.

Substituted alkylaromatic bodies give *substituted acids*.

$$\underset{\text{Nitrotoluenes}}{NO_2C_6H_4CH_3} \longrightarrow \underset{\text{Nitrobenzoic acids}}{NO_2C_6H_4COOH,}$$

$$\underset{\text{Tolylsulphonic acid}}{CH_3C_6H_4SO_3H} \longrightarrow \underset{\text{Sulphobenzoic acid}}{C_6H_4<^{COOH}_{SO_3H}}$$

But the cresols (hydroxytoluenes, $HOC_6H_4CH_3$) do *not* give the corresponding hydroxybenzoic acids.

β. In acid solution.

This is less generally used, its effect being quite similar to that of acid dichromate, this satisfying all requirements in general.

d. **Solns. of Copper Salts.**

α. Copper solns., alkaline, *e.g.* Fehling's Soln.

This oxidises *fatty aldehydes*, simple and complex, also *fatty hydroxyketones* (complex), *i.e.* the *sugars*. The simple *aldehydes* pass into corresponding *acids*, but with the sugars the reaction is much more complex. Aromatic aldehydes are not affected in this manner by Fehling's Soln.

Alkyl and *aryl hydrazines* give *hydrocarbon* and nitrogen.

$$\underset{\text{Phenylhydrazine}}{C_6H_5N_2H_3} + 2CuO = \underset{\text{Benzene}}{C_6H_6} + N_2 + H_2O + Cu_2O,$$

$$\underset{\text{Methylhydrazine}}{CH_3N_2H_3} + 2CuO = \underset{\text{Methane}}{CH_4} + N_2 + H_2O + Cu_2O.$$

β. Copper acetate with acetic acid.

This is useful for the differentiation of certain sugars. Thus, glucose is oxidised, lactose is not, but both are oxidised by Fehling's Soln.

e. **Silver Oxide, ammoniacal:** Tollens' Reagent.

This oxidises *simple aldehydes, fatty* and *aromatic*, into *acids*, *complex hydroxy-aldehydes* and *-ketones* (*i.e.* sugars) more completely, with formation of a silver mirror.

$$\underset{\text{Acetaldehyde}}{CH_3HCO} + Ag_2O = \underset{\text{Acetic acid}}{CH_3COOH} + 2Ag.$$

$$\underset{\text{Benzaldehyde}}{C_6H_5HCO} + Ag_2O = \underset{\text{Benzoic acid.}}{C_6H_5COOH} + 2Ag.$$

Formates and tartrates are similarly oxidised.

$$\underset{\text{Formate}}{HCOONa} + Ag_2O = \underset{\text{Bicarbonate}}{HOCOONa} + 2Ag.$$

Citrates are oxidised, but produce no mirror.

f. **Ferric Chloride,** neutral soln., *i.e.* containing no free acid.

Some of the colour reactions given by this are known to be oxidations.

Hydroquinone gives benzoquinone, passing through quinhydrone as an intermediate stage.

$$\underset{\text{colourless}}{C_6H_4(OH)_2(p)} \longrightarrow \underset{\text{green}}{C_6H_4O_2 . C_6H_4(OH)_2} \longrightarrow \underset{\text{yellow-red}}{C_6H_4O_2}.$$

α-Naphthol, $C_{10}H_7OH$, precipitates violet flakes of *α*-dinaphthol, $C_{20}H_{12}(OH)_2$.

β-Naphthol, $C_{10}H_7OH$, precipitates a green powder of *β*-dinaphthol, $C_{20}H_{12}(OH)_2$.

Aromatic primary amines give *quinones* in the end. Other aromatic *amines* give more or less characteristic *coloured products* : also, most *tertiary (OH) bodies*, especially aromatic ones, *phenols*, *naphthols*. Some "enolic" fatty bodies do so too, *e.g.* ethyl acetoacetate.

Hydrazines, aryl and *alkyl* give *hydrocarbon* and *nitrogen*.

$$\underset{\text{Phenylhydrazine}}{C_6H_5N_2H_3} + 2FeCl_3 = \underset{\text{Benzene}}{C_6H_6} + N_2 + 2HCl + 2FeCl_2.$$

g. **Nitric Acid, Nitrates.**

a. Nitric acid, conc. and dil.

The conc. acid is not in general available for the oxidation of aromatic cpds., since it causes nitration, but :—

$$\underset{\text{Indigo}}{C_{16}H_{10}N_2O_2} \quad \underset{\text{gives}}{\longrightarrow} \quad \underset{\text{Isatin.}}{2C_8H_5NO_2.}$$

$$\underset{\text{Benzoin}}{C_6H_5CHOH,CO,C_6H_5} \quad \underset{\text{gives}}{\longrightarrow} \quad \underset{\text{Benzil.}}{C_6H_5CO.COC_6H_5.}$$

Many *fatty OH bodies* give *oxalic acid* as end product, *e.g.* ethyl alcohol, other alcohols and some sugars, *e.g.* glucose and sucrose.

Ethyl alcohol also gives glycollic acid ; glycerol, glyceric acid.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \longrightarrow \underset{\text{Glycollic acid}}{CH_2OH,COOH} \longrightarrow \underset{\text{Oxalic acid}}{(COOH)_2}.$$

Under other conditions, nitrates, *e.g.* ethyl nitrate, "nitroglycerine," are formed.

$$\underset{\text{Glycerol}}{CH_2OH.CHOH.CH_2OH} \longrightarrow \underset{\text{Glyceric acid}}{CH_2OH.CHOH.COOH}$$

In some cases, *tertiary hydrocarbons* pass into *alcohols*.

$$R_3CH \longrightarrow R_3C(OH), \quad | \quad (C_6H_5)_3CH \longrightarrow (C_6H_5)_3COH.$$

Tertiary HC — Tertiary alcohol | Triphenylmethane — Triphenyl carbinol

The dilute acid converts *alkylaromatic bodies* into *acids*.

$$\left.\begin{array}{l} \underset{\text{Toluene}}{C_6H_5CH_3} \longrightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} \\ \underset{\text{Ethylbenzene}}{C_6H_5CH_2CH_3} \longrightarrow \underset{\text{Phenylacetic acid}}{C_6H_5CH_2COOH} \end{array}\right\} \text{slowly, however.}$$

Mesitylene $CH_3 \langle \text{ring} \rangle (CH_3)_2 \longrightarrow HOOC \langle \text{ring} \rangle (COOH)_2$ Trimesic acid.

β. Nitrates of reducible metals, such as lead, copper.

These hydrolyse and oxidise *halogen esters* into *aldehydes*.

$$\underset{\text{Benzyl chloride}}{2C_6H_5CH_2Cl} + Pb(NO_3)_2 = \underset{\text{Benzaldehyde}}{2C_6H_5HCO} + PbCl_2 + H_2O + \text{“}N_2O_3.\text{”}$$

h. **Atmospheric Oxygen with "carriers"** at ordinary temperature.

a. Air and moisture, water acting here as carrier (through H_2O_2).

Aldehydes slowly pass into *acids*.

$$\underset{\text{Acetaldehyde}}{CH_3HCO} + O = \underset{\text{Acetic acid}}{CH_3COOH.}$$

Mixture becomes acid.

$$\underset{\text{Benzaldehyde}}{C_6H_5HCO} + O = \underset{\text{Benzoic acid}}{C_6H_5COOH.}$$

A solid deposit forms.

Alkylates slowly come to contain *aldehyde resin* and *salt* of corresponding *acid*.

$$\underset{\text{Alkylate}}{RCH_2ONa} \longrightarrow \underbrace{\underset{\text{Aldehyde}}{RHCO} + \underset{\text{Alkali}}{NaOH}}_{\text{Forming Aldehyde Resin}} \longrightarrow \underset{\text{Salt of acid}}{RCOONa}$$

β. Air or oxygen with platinum black.

Alcohols may pass into *aldehydes* or *ketones*, and *aldehydes* further into *acids*, as in the "Quick Vinegar Process." Compare acetic fermentation.

$$\underset{\text{Alcohol (primary)}}{RCH_2OH} \longrightarrow \underset{\text{Aldehyde}}{RHCO} + H_2O, \text{ or } \longrightarrow \underset{\text{Acid}}{RCOOH} + H_2O$$

$$\underset{\text{Alcohol (secondary)}}{RR'CHOH} \longrightarrow \underset{\text{Ketone}}{RR'CO,}$$ Action no further in this case, and in any case slow.

γ. Air or oxygen in presence of alkalis.

This case occurs easily with *di-* and *poly-* *(OH) benzene derivatives*, these giving *coloured tarry bodies*, sometimes with characteristic colours.

Catechol gives a green, then a brown, then a black colour.

Pyrogallol + KOH, used in estimating free oxygen, gives CO_2, acetic acid and brown substances, as also does gallic acid.

j. **Red Hot Copper Oxide,** with or without air or oxygen, oxidises all carbon cpds. into water and carbon dioxide. In presence of some metallic copper, any nitrogen oxides formed are reduced to nitrogen. This, with other necessary modifications, is the method of ultimate quantitative analysis, *i.e.* "Combustion," for C and H, and for N by the absolute method.

k. **Bleaching Powder,** or hypochlorites in alkaline soln.

The colour reactions given by certain *aromatic* bodies, e.g. *amines*, with bleaching powder, are probably due to oxidation, in part at any rate (see also V. *b*.).

l. **Chromic Acid** (*i.e.* anhydride) in glacial acetic acid.

This is used very generally in the oxidation of bodies insol. in water. It may, however, be too powerful for some cases, *e.g.* benzene, giving CO_2 and H_2O, slowly however.

Complex *aromatic hydrocarbons* give *quinones*.

Anthracene, $C_{14}H_{10}$ and phenanthrene $C_{14}H_{10}$ give anthra- and phenanthra-quinones $C_{14}H_8O_2$. Similarly, naphthalene gives naphthoquinone, $C_{10}H_8 \longrightarrow C_{10}H_6O_2$.

Chromyl chloride, CrO_2Cl_2, is a rather dangerous oxidising agent and has therefore a rather restricted application.

It goes most quietly in CS_2 soln., and is applied in the oxidation of *alkylaromatic hydrocarbons* into *aromatic aldehydes* (Étard). A double cpd. is formed and ppd. On mixing this with water, the aldehyde separates.

$$\underset{\text{Chromyl chloride}}{2CrO_2Cl_2} + \underset{\text{Toluene}}{PhCH_3} \longrightarrow \underset{\text{brown pp.}}{PhCH_3(CrO_2Cl_2)_2}$$

$$+ H_2O \longrightarrow \underset{\text{Benzaldehyde}}{PhHCO} + CrCl_3 + CrO_3 + H_2O.$$

m. **Ferricyanide (Potassium)** with **Alkali.**

Alkylaromatic hydrocarbons pass into *acids*.

$$\underset{\text{Toluene}}{C_6H_5CH_3} + \underset{\text{Ferricyanide}}{6K_3FeCy_6} + 7KOH$$

$$= \underset{\text{Benzoate}}{C_6H_5COOK} + \underset{\text{Ferrocyanide}}{6K_4FeCy_6} + 5H_2O.$$

n. **Manganese Dioxide** with **Acid,** dil. sulphuric.

Primary alcohols give *aldehydes,* and ethers of these, the *acetals*.

$$\underset{\text{Ethyl alcohol}}{CH_3H_2COH} \longrightarrow \underset{\text{Aldehyde}}{CH_3HCO} \longrightarrow \underset{\substack{\text{Ethylidene diethyl ether}\\ = \text{Acetal itself}}}{CH_3HC(OC_2H_5)_2}.$$

o. **Lead Dioxide,** neutral, alkaline, or acid.

Ferrocyanides pass into *ferricyanides* in neutral soln., *i.e.* with a current of CO_2 to neutralise the bases.

$$\underset{\text{Ferrocyanide}}{2K_4FeCy_6} + PbO_2 + 3H_2CO_3$$

$$= \underset{\text{Ferricyanide}}{2K_3FeCy_6} + 2KHCO_3 + PbCO_3 + 2H_2O.$$

p. **Caustic Alkalis at high temperatures** cause oxidation, hydrogen being evolved, often oxidised by oxygen from the air.

Cellulose gives oxalates (manufactured from sawdust).
Phenol gives diphenols $C_{12}H_8(OH)_2$.

CHAPTER II.

REDUCTION.

TYPES OF REDUCTION.

This may be considered the reverse of oxidation. It may take the following forms :—

1. Addition of hydrogen, with subsequent and consequent elimination of water.

$$C_6H_5NO_2 + 3H_2 = C_6H_5NH_2 + 2H_2O.$$

Nitrobenzene — Aniline

$$C_6H_5IO_2 + 2H_2 = C_6H_5I + 2H_2O.$$

Iodoxybenzene — Iodobenzene

This is the characteristic reaction for nitro compounds.

2. Addition of hydrogen without elimination of water.

$$CH_3HCO + H_2 = CH_3CH_2OH.$$

Acetaldehyde — Ethyl alcohol

$$C_6H_4O_2 + H_2 = C_6H_4(OH)_2.$$

Benzoquinone — Hydroquinone

3. Addition of hydrogen to unsaturated bodies.

Here, however, there need be no rupture of the molecule, as in the case where oxygen is added. (See III. *f*.)

$$H_2C : CH.COOH + H_2 = CH_3CH_2COOH.$$

Acrylic acid — Propionic acid

$$PhCH : CHCOOH + H_2 = PhCH_2CH_2COOH.$$

Cinnamic acid — Phenylpropionic acid

4. Removal of (HO), that is, reduction with dehydration.

This case is of somewhat limited occurrence unless the reduction of acid to aldehyde be considered a case in point, this not being a direct reduction.

$$\underset{\text{Acetic acid}}{CH_3COOH} + H_2 \left[= \underset{\text{Ethylidene glycol}}{CH_3HC(OH)_2} \right] = \underset{\text{Acetaldehyde}}{CH_3HCO} + H_2O.$$

This is carried out by indirect means.

So also sulphonic chloride to mercaptan.

$$RSO_2Cl + 3H_2 = RSH + 2H_2O + HCl.$$

5. Direct removal of oxygen.

$$\underset{\text{Phenol}}{C_6H_5OH} + Zn = \underset{\text{Benzene}}{C_6H_6} + ZnO.$$

$$\underset{\text{Azoxybenzene}}{4(C_6H_5)_2N_2O} + 3Fe = \underset{\text{Azobenzene}}{4(C_6H_5)_2N_2} + Fe_3O_4.$$

6. Replacement of halogen by hydrogen, the reverse of halogenation (see V). This comes naturally here, because the appropriate reagents for the above can effect this also.

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + H_2 = \underset{\text{Ethane}}{C_2H_6} + HBr.$$

This reaction has reached its limit, of course.

$$\underset{\text{Brombenzene}}{C_6H_5Br} + H_2 = \underset{\text{Benzene}}{C_6H_6} + HBr.$$

This reaction can go further into di-, tetra-, and hexahydrobenzene.

This is the easiest method for identifying halogens in organic bodies, the halogens remaining as metallic salts.

Reducing Agents.

The reagents most commonly used, and examples of their application, are given below.

a. **Zinc dust** at a **red heat** reduces nearly all organic bodies, in many cases completely. The hydrogen required in some cases

comes from the hydroxide generally present in ordinary samples of zinc dust.

$$\underset{\text{Phenol}}{C_6H_5OH} + Zn = \underset{\text{Benzene}}{C_6H_6} + ZnO.$$

$$\underset{\text{Alizarin}}{C_{14}H_6O_2(OH)_2} + 5Zn + Zn(OH)_2 \longrightarrow \underset{\text{Anthracene}}{C_{14}H_{10}} + 6ZnO.$$

$$\underset{\text{Succinimide}}{\begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix} \Big> NH} + 2Zn \longrightarrow \underset{\text{Pyrrol}}{\begin{matrix} CH : CH \\ | \\ CH : CH \end{matrix} \Big> NH} + 2ZnO.$$

b. **Stannous Chloride, Stannites.**

α. Stannous chloride in presence of acids, *e.g.* HCl.

Sometimes more useful than (*c*), *e.g.* in proving the presence of *nitro groups*, by the oxidation of the $SnCl_2$ added drop by drop (by change in colour of H_2S pp.); or in alcoholic solution, giving step by step reduction of *polynitro* cpds.

$$\underset{\text{Dinitrotoluene}}{CH_3C_6H_3(NO_2)_2} + 3SnCl_2 + 6HCl$$

$$= \underset{\text{Aminonitrotoluene}}{CH_3C_6H_3 < \begin{matrix} NO_2 \\ NH_2 \end{matrix}} + 3SnCl_4 + 2H_2O.$$

Diazo-bodies give *Hydrazines* (aq. solution and HCl).

$$\underset{\text{Diazo-body}}{N : N < \begin{matrix} Ph \\ Cl \end{matrix}} + 2SnCl_2 + 4HCl = \underset{\text{Phenylhydrazine salt}}{NH_2.NHPh.HCl} + 2SnCl_4.$$

β. Stannites, *i.e.* $SnCl_2$ and excess caustic soda.

Nitroaromatic bodies give *Azo-bodies*.

$$\underset{\text{Nitrobenzenesulphonic}}{2NO_2C_6H_4SO_3H} + 4SnCl_2 + 18NaOH$$

$$= \underset{\text{Azobenzenesulphonic}}{N_2(C_6H_4SO_3Na)_2} + 4Na_2SnO_3 + 8NaCl + 10H_2O.$$

Diazo-bodies pass into *hydrocarbons*.

$$\underset{\text{Ph. diazon. chlor.}}{N : N < \begin{matrix} Ph \\ Cl \end{matrix}} + SnCl_2 + 5NaOH$$

$$= N_2 + \underset{\text{Benzene}}{C_6H_6} + Na_2SnO_3 + 3NaCl + 2H_2O.$$

c. **Tin, metallic.**

α. The metal and acid: conc. hydrochloric.

The reagent for the reduction, on a laboratory scale, of *aromatic nitro cpds.* to *amino cpds.*

$$2CH_3C_6H_4NO_2 + 3Sn + 14HCl = 2CH_3C_6H_4NH_3Cl + 3SnCl_4 + 4H_2O.$$

Nitrotoluene — Toluidinium chloride

$$2NO_2C_6H_4COOH + 3Sn + 12HCl = 2NH_2C_6H_4COOH + 3SnCl_4 + 4H_2O.$$

Nitrobenzoic acid — Aminobenzoic acid

Also for the reduction of *nitrous* and *nitric* esters, hydroxylamine being produced—and an alcohol.

$$C_2H_5ONO + Sn + 5HCl = C_2H_5OH + HONH_3Cl + SnCl_4$$

Ethyl nitrite — Ethyl alcohol — Hydroxylamine salt

The amine bases formed in the above cases remain as HCl salts or double salts, the bases being set free and the tin eliminated, as stannate, by adding excess of NaOH *e.g.*

β. Tin and alkalis, *e.g.* NaOH.

This may often replace zinc with advantage in cases where the elimination of the metal might be complicated.

d. **Zinc, granulated or foil.**

α. Zinc and dilute hydrochloric or sulphuric.

This has almost the same range of applicability as tin and acids, but has the advantage of not requiring conc. acids. The Sn may be removed by a current of H_2S directly, the Zn by H_2S only after the addition of sodium acetate, or by precipitation with sodium carbonate. It is seldom used for substs. insol. in water or dil. acids.

β. Zinc and dil. acetic acid.

This is convenient because of the easy removal of the Zn by H_2S.

$$2C_6H_5COC_6H_5 + Zn + 2HOAc = (C_6H_5)_2C(OH)C(OH)(C_6H_5)_2 + Zn(OAc)_2.$$

Benzophenone — Benz-pinacone

γ. Zinc and alkalis, aqueous or alcoholic.

$$\underset{\text{Benzophenone}}{C_6H_5COC_6H_5} + Zn + 2NaOH = \underset{\text{Diphenylcarbinol}}{C_6H_5CHOHC_6H_5} + \underset{\text{"Zincate"}}{Zn(ONa)_2}.$$

The zinc here is removed by a current of CO_2.

c. **Zinc dust in wet way.**

a. Zinc dust in neutral soln.

Aromatic nitro bodies give *hydroxylamine derivatives.*

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 2Zn + 3H_2O = \underset{\text{Phenylhydroxylamine}}{C_6H_5NHOH} + 2Zn(OH)_2.$$

Used in presence of calcium chloride.

Azo compounds give *amino compounds.*

$$\underset{\text{Azobenzene}}{(C_6H_5)_2N_2} + 2Zn + 4H_2O$$

$$= \underset{\text{Aniline}}{2C_6H_5NH_2} + 2Zn(OH)_2 \text{ used as above.}$$

β. Zinc dust in alkaline solns., *e.g.* caustic soda.

Nitroaromatic bodies give *azobodies.*

$$\underset{\text{Nitrotoluene (m)}}{2CH_3C_6H_4NO_2} + 4Zn + 8NaOH$$

$$= \underset{\text{Azotoluene (m)}}{(CH_3C_6H_4)_2N_2} + 4Zn(ONa)_2 + 4H_2O.$$

γ. Zinc dust and acids, generally acetic—a reducing agent of very general application.

$$\underset{\text{Benzaldehyde}}{C_6H_5HCO} + Zn + 3HOAc$$

$$= \underset{\text{Benzyl acetate}}{C_6H_5CH_2OCOCH_3} + Zn(OAc)_2 + H_2O.$$

δ. Zinc dust and ammonia.

This mixture *removes halogen* from halogen cpds. *without adding hydrogen,* i.e. it leaves unsaturated cpd.

$$\underset{\text{Ethylene dibromide}}{C_2H_4Br_2} + Zn + xNH_3 = \underset{\text{Ethylene}}{C_2H_4} + \underset{\text{Zinc bromide ammonia cpd.}}{ZnBr_2,xNH_3}$$

Diazo cpds. give corresponding *hydrazines.*

$$2N:N<\begin{matrix}Ph\\Cl\end{matrix}+4Zn+6H_2O$$
Diazo chloride

$$=\underset{\text{Hydrazine}}{2PhN_2H_3}+\underbrace{ZnCl_2+3Zn(OH)_2}_{\text{sol. in ammonia}}$$

Using aqueous ammonia.

ε. Zinc-Copper couple.

This can be used similarly to zinc dust (above) with similar results. But with alcohol it forms the original method (of Gladstone and Tribe) for reducing *alkyl halides* to their *hydrocarbons.*

$$\underset{\text{Ethyl iodide}}{2C_2H_5I}+2Zn+2EtOH=\underset{\text{Ethane}}{2C_2H_6}+ZnI_2+Zn(OEt)_2.$$

$$\underset{\text{Chloracetic acid}}{2CH_2ClCOOH}+2Zn=\underset{\text{Zinc acetate}}{(CH_3COO)_2Zn}+ZnCl_2.$$

f. **Sodium, Potassium.**

α. Sodium, etc., in presence of water: substs. sol.

Alcohols: primary from *aldehydes, secondary* from *ketones.*

$$\underset{\text{Acetaldehyde}}{CH_3HCO}+2H_2O+2Na=\underset{\text{Ethyl alcohol}}{CH_3CH_2OH}+2NaOH.$$

$$\underset{\text{Benzaldehyde}}{PhHCO}\text{ similarly}\rightarrow\underset{\text{Benzyl alcohol.}}{PhCH_2OH.}$$

$$\underset{\text{Acetone}}{CH_3COCH_3}+2H_2O+2Na=\underset{\text{Isopropyl alcohol}}{(CH_3)_2CHOH}+2NaOH.$$

$$\underset{\text{Benzophenone}}{Ph_2CO}\text{ similarly}\rightarrow\underset{\text{Benzhydrol}}{Ph_2CHOH.}$$

β. Sodium, etc., in presence of alcohols, methyl or ethyl, —or amyl where slower action or higher temperature is required.

For substs. insol. in water, e.g. *halogen derivatives.*

$$\underset{\text{Alcohol}}{2C_2H_5OH}+2Na=\underset{\text{Alkylate}}{2C_2H_5ONa}+H_2\text{ with }\underset{\text{Ethyl bromide}}{C_2H_5Br}\text{ gives }\underset{\text{Ethane}}{C_2H_6}$$

and HBr.

$$\text{Then }HBr+\underset{\text{Alkylate}}{NaOEt}=NaBr+\underset{\text{Alcohol}}{EtOH.}$$

Similarly C_6H_5Br, phenyl bromide, gives benzene and NaBr.

These are cases of reverse substitution of course, *i.e.* replacement of a halogen by hydrogen.

This reagent often causes the addition of hydrogen to unsaturated bodies, even those which do not in general behave as unsaturated, *e.g.* benzene ring cpds. See Reaction III *f*.

Cyanides, *i.e.* nitriles of the acids, give higher *primary amines*.

$$\underset{\text{Ethylcyanide or propionitril}}{C_2H_5CN} + 2H_2 \longrightarrow \underset{\text{Propylamine}}{C_2H_5CH_2NH_2}.$$

$$\underset{\text{Cyanogen}}{C_2N_2} + 4H_2 = \underset{\text{Ethylenediamine}}{(CH_2NH_2)_2}.$$

Sodium amalgam (α) (β) as above, where a less energetic reaction is required.

In presence of water acetone gives isopropyl alcohol, and if there be not enough hydrogen, *i.e.* if the amalgam be of poor quality, some pinacone is formed. Similarly for other ketones.

$$\underset{\text{Acetone}}{2CH_3COCH_3} + 2H_2 = \underset{\text{Isopropyl alcohol}}{2CH_3CHOHCH_3}$$

$$\text{or} \qquad + H_2 = \underset{\text{Pinacone}}{(CH_3)_2COH.COH(CH_3)_2}.$$

Similarly glyoxylic acid may give tartaric, *i.e.* racemic acid.

$$\underset{\text{Glyoxylic}}{2HCO.COOH} + 2Na = \underset{\text{Racemic acid (salt of)}}{(HCOH)_2(COONa)_2}.$$

g. **Potash or Soda, alcoholic,** and **alkylates,** potassium or sodium, in alc. soln.

These are applied in reducing aromatic *nitrobodies* to *azoxybodies*.

$$\underset{\text{Nitrobenzene}}{4C_6H_5NO_2} + \underset{\text{Methoxide}}{3CH_3ONa} = \underset{\text{Azoxybenzene}}{2(C_6H_5)_2N_2O} + \underset{\text{Formate}}{3HCOONa} + 3H_2O.$$

h. **Formates, metallic.**

Salts of *acids* heated with dry formates give *aldehydes*.

$$\begin{array}{lll} \text{Acetate} & CH_3CO \mid Oba & \\ \text{Formate} & H \mid CO\ Oba & \longrightarrow \underset{\text{Acetaldehyde}}{CH_3HCO} + BaCO_3. \end{array}$$

The metals must form stable carbonates.

When formates of these metals are heated by themselves, they give formaldehyde; salts of other fatty acids similarly give ketones, under reduced pressure if necessary.

j. **Hydriodic acid** at high temperatures and pressures, as in a sealed tube, *i.e.* the gas HI, causes fairly complete reduction (see *f.*).

Fatty (OH) or (O) cpds. give corresponding *alkyl iodide.*

$$\underset{\text{Mannitol}}{C_6H_{14}O_6} + 11HI = \underset{\text{Hexyl iodide (iso)}}{C_6H_{13}I} + 6H_2O + 5I_2.$$

$$\underset{\text{Glycerol}}{CH_2OHCHOHCH_2OH} + 6HI = \underset{\text{Propane}}{C_3H_8} + 3I_2 + 3H_2O.$$

Unsaturated ring hydrocarbons, etc., give *saturated ring hydrocarbons.*

$$\underset{\text{Benzene}}{C_6H_6} + 6HI = \underset{\text{Hexahydrobenzene}}{C_6H_{12}} + 3I_2.$$

$$\underset{\text{Aniline}}{C_6H_5NH_2} + 8HI = \underset{\text{Hexamethylene}}{C_6H_{12}} + H_3N + 4I_2.$$

The reason why substitution by iodine does not succeed under the same simple conditions as with chlorine and with bromine is that the HI simultaneously formed acts as reducing agent on the expected product. In presence of substs. which can destroy this HI, the reaction goes normally.

$$\underset{\text{Ethane}}{2C_2H_6} + 2I_2 + HgO = \underset{\text{Ethyl iodide}}{C_2H_5I} + HgI_2 + 3H_20.$$

$$\underset{\text{Ethane}}{5C_2H_6} + 2I_2 + \underset{\text{Iodic acid}}{HIO_3} \longrightarrow \underset{\text{Ethyl iodide}}{5C_2H_5I} + 3H_2O.$$

k. **Phosphorus and Iodine: Phosphonium Iodide.**

The action here is the same as that of HI, and the range of application rather wider: method the same.

Higher fatty acids give corresponding *hydrocarbons*, the phosphorus remaining in the form of oxyacid.

Nonylic acid gives nonane and phosphorous acid.

$$C_8H_{17}COOH + 2P + 3I_2 + 4H_2O = C_8H_{17}CH_3 + 2H_3PO_3 + 3I_2.$$

Alkylaromatic ketones give corresponding *hydrocarbons.*

$$\underset{\text{Acetophenone}}{3C_6H_5COCH_3} + P_4 + 6I_2 + 9H_2O = \underset{\text{Ethylbenzene}}{3C_6H_5CH_2CH_3} + 6I_2 + 4H_3PO_3.$$

Hydroxy bodies, fatty and aromatic, give *hydrocarbons.*

$$\underset{\text{Ethyl alcohol}}{8C_2H_5OH} + \underset{\text{Phosphonium iodide}}{2PH_4I} = \underset{\text{Ethane}}{8C_2H_6} + \underset{\text{Phosphoric acid}}{2H_3PO_4} + I_2 + H_2O.$$

l. **Iron** (filings, borings) ; **ferrous** salts.

a. Iron filings, in the dry way.

The only common case is the reduction of axoxybenzene to azobenzene.

$$4(C_6H_5)_2N_2O + 3Fe = 4(C_6H_5)_2N_2 + Fe_3O_4.$$

β. Iron in presence of acids.

Often applied on a manufacturing scale (for obvious reasons), as in reducing *aromatic nitro compounds* to *amines.* It is not merely the nascent hydrogen which reduces, since it is found in practice that much less acid than that equivalent to the iron is really necessary. Thus, using acetic in manufacture of aniline,

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + \underset{\text{Ferrous acetate}}{6Fe(OAc)_2} + 6HOAc = \underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Ferric acetate}}{6Fe(OAc)_3} + 2H_2O.$$

Then $2Fe(OAc)_3 + Fe = 3Fe(OAc)_2$ and so on again.

γ. Ferrous salts in alkaline solution (*i.e.* $Fe(OH)_2$).

Picric acid gives *picramic acid.*

$$HOC_6H_2(NO_2)_3 + 4H_2O + 6Fe(OH)_2 = HOC_6H_2NH_2(NO_2)_2 + 6Fe(OH)_3.$$

m. **Sulphurous Acid.**

This has not many applications, but it is used for the conversion of *para-quinones* into *para-dihydroxy bodies*.

$$\underset{\text{Benzoquinone}}{C_6H_4O_2} + H_2O + H_2SO_3 = \underset{\text{Hydroquinone}}{C_6H_4(OH)_2} + H_2SO_4$$

n. **Ammonium Sulphide, alcoholic,** *i.e.* ammonia, alcohol, and a current of H_2S.

Aromatic nitro cpds. are reduced to *amino* cpds., step by step, each NO_2 group being a separate stage.

$$\underset{\text{Dinitrobenzene}}{C_6H_4 < {NO_2 \atop NO_2}} + 3H_2S = \underset{\text{Nitraniline}}{C_6H_4 < {NO_2 \atop NH_2}} + 2H_2O + 3S$$

$$\text{then } + 6H_2S \text{ to } \underset{\text{Phenylenediamine}}{C_6H_4 < {NH_2 \atop NH_2}} \text{ etc.}$$

CHAPTER III.

THE ADDITION REACTION AS SHOWING UNSATURATION.

The term *unsaturation* is used to denote the state of a cpd., which forms new cpds. by addition, *i.e.* by combining with the whole of a new molecule, or with more than one similar molecule, as contrasted with the formation of new cpds. only by an interchange of atoms or atomic groups in the two molecules, *i.e.* substitution.

Case 1.—A molecule of an unsaturated compound may add on one molecule made up of two monad groups, such as Br-Br, HI CH_3I, etc. Sulphuric acid and water are added on in the forms $H.SO_4H$ and H.OH respectively.

This is the behaviour of cpds. belonging to the Olefine or Ethylene series—said to possess one double linkage, *e.g.* $CH_2 : CH_2$.

Case 2.—A molecule may add on two such molecules, the same or different, simultaneously or successively.

This is the behaviour of cpds. belonging to the Acetylene series—said to possess one triple linkage, *e.g.* HC : CH, acetylene.

The behaviour of these with ammoniacal cuprous chloride soln. (see IV) may be considered in certain cases as an example of this kind, cp. $C_2H_2.Cu_2O$; in other cases it must be considered as a substitution property due to the presence of the group C : CH, as cpds. of the type RC : CR do not react so.

Substs. of the type $\left.\begin{matrix}R\\ or\\ H\end{matrix}\right\} CH : C : CH \left\{\begin{matrix}R\\ or\\ H\end{matrix}\right.$ and others, similarly

containing two double linkages, also add on $2Br_2$, 2HBr, etc., but these in no case react with ammoniacal cuprous chloride.

In a number of cases addition reactions happen, which must be due to the linkage of other elements than carbon and hydrogen. In this sense any multiple linkage may be considered unsaturated. Thus, cpds. containing the grouping $> C:O$ (aldehydes and ketones) show addition reactions, as with $H.NH_2$, H.OH, H.CN, HSO_3Na, and in many cases of condensation and hydrolysis (see VII., IX., and XIV.), addition of this kind may precede the elimination of the water or HX group. Acids, which also contain the $> CO$ group, do not show this unsaturation unless the existence of unstable "ortho" acids, *e.g.* $CH_3C(OH)_3$ as in aq. soln. (stable esters being known) and the existence of unstable vapour molecules (*e.g.* $(C_2H_4O_2)_2$ at 150°) be considered cases in point.

Sulphur cpds., owing to the possibilities of higher valencies than 2 for that element, often give the reactions characteristic of unsaturated bodies, *e.g.* thioethers RSR′ combine with Br_2, as indeed, and probably for the same reason, do some similar oxygen cpds., *e.g.* methyl ether forms $(CH_3)_2O.HCl$. and γ-pyrone derivatives form salts as N-bases do, *e.g.*

$$OC < \begin{matrix} CH:CMe \\ CH:CMe \end{matrix} > O.HCl.$$

The formation of salts by substituted ammonias (of all classes, nitriles included) is due to the original trivalency of the N atom becoming pentavalency. So also is the addition of one, two, or three CH_3I, etc., molecules by tertiary, secondary or primary bases, forming HI salts of quaternary bases and eliminating the rest of the HI.

Addition of some molecules, *e.g.* HCl, H.OH, is brought about with greater difficulty than in other cases, which might seem quite similar, as HI. This is due to the fact that in such addition the added atoms or groups must pass to different parts of the unsaturated molecule, and therefore must themselves part company.

Carbon unsaturation may occur in all groups of organic cpds., hydrocarbons, alcohols, acids, etc. It is detected by:—

THE ADDITION REACTION.

a. The unsaturated subst. adds on **Bromine**, 2, 4, or 6, etc., atoms.

This is more convenient, if less easy, than the addition of

chlorine. The products are *consecutive* di-, tetra-, etc., *bromo-derivatives* (generally; see end of this chapter).

$HC : CH + Br_2 = HCBr{:}CHBr$ and another $Br_2 \longrightarrow CHBr_2.CHBr_2.$

Acetylene — Acetylene dibromide, symmetrical dibromethylene — Acetylene tetrabromide, symmetrical tetrabromethane

$H_2C : CHCOOH + Br_2 = CH_2BrCHBrCOOH.$

Acrylic acid — αβ-Dibrompropionic acid

$H_2C : CHCH_2OH + Br_2 = CH_2BrCHBrCH_2OH.$

Allyl alcohol — αβ-Dibrompropyl alcohol

$PhCH : CHCOOH + Br_2 = PhCHBr.CHBrCOOH.$

Cinnamic acid — Dibromcinnamic acid

b. The unsaturated subst. adds on **hydrogen bromide,** 1, 2, etc., molecules.

This is more convenient, if less easy, than the addition of hydrogen iodide; more easy, if less convenient, than the addition of hydrogen chloride. The products are various *saturated halogen cpds.*

$HC : CH + HBr = H_2C{:}CHBr$ and another $HBr \longrightarrow BrCH_2.CH_2Br$

Acetylene — Vinyl bromide — Ethylene dibromide

$H_2C{:}CHCOOH + HBr = H_2BrC.CH_2.COOH.$

Acrylic acid — β-Brompropionic acid

$PhCH{:}CHCOOH + HBr = PhCHBr.CH_2.COOH.$

Cinnamic acid — Phenyl β-brompropionic

$HC : C.COOH + HBr = HCBr.CHCOOH$

Propiolic acid — β-Bromacrylic acid

with another $HBr \longrightarrow H_2CBrCHBrCOOH.$

αβ-Dibrompropionic acid

c. **Sulphuric Acid** is added in the form $H.SO_4H$.

Ethylenes give *alkylsulphuric acids,* with one molecule H_2SO_4.

$H_2C{:}CH_2 + HSO_4H = H_3C.CH_2SO_4H.$

Ethylene — Ethylsulphuric acid

$H_2C{:}CHCOOH + HSO_4H = H_2C(SO_4H)CH_2COOH.$

Acrylic acid — β-Sulphopropionic acid

Acetylenes give *alkylidene* sulphuric acids, with two molecules H_2SO_4, since the first recognisable product after hydrolysis is acetaldehyde.

$$\underset{\text{Acetylene}}{HC \vdots CH} + 2HSO_4H$$

$$= \underset{\text{Ethylidene disulphuric acid}}{H_3C.HC(SO_4H)_2} \longrightarrow \underset{\text{Aldehyde}}{CH_3HCO} \; [\text{from } \underset{\text{unstable}}{CH_3HC(OH)_2}],$$

$$\text{or } \underset{\text{Acetylene}}{HC \vdots CH} + HSO_4H = \underset{\text{Vinylsulphuric acid}}{H_2C{:}HCSO_4H} \longrightarrow \underset{\text{Vinyl alcohol}}{H_2C{:}HCOH} + H_2O$$

$$H_2C : HCOH + H_2O \; [= \underset{\text{Ethylidene glycol}}{H_3CHC(OH)_2}] \longrightarrow CH_3HCO.$$

The unstable vinyl alcohol passes into (isomeric) acetaldehyde.

d. The subst. adds on **water** in the form H.OH—**Hydration**.

This in general needs some outside assistance, *e.g.* high temperature and pressure, as in a sealed tube: in some cases, however, it happens unassisted, especially where the unsaturation is not entirely C-unsaturation.

$$\underset{\text{Acrylic acid}}{H_2C{:}CHCOOH} \longrightarrow \underset{\text{Hydracrylic acid, } \beta \text{ (HO) propionic}}{HOCH_2.CH_2COOH.}$$

$$\underset{\text{Isobutylene}}{Me_2C{:}CH_2} + H_2O \longrightarrow \underset{\substack{\text{Trimethyl carbinol}\\ \text{Tertiary butyl alcohol}}}{Me_2C(OH).CH_3.}$$

$$\underset{\text{Succinic anhydride}}{\begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix}\!\!>\!O} + \begin{matrix} H \\ \cdot \\ OH \end{matrix} \longrightarrow \underset{\text{Succinic acid}}{\begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix}}$$

Hydration probably always precedes hydrolysis. See IX.

e. **Hypochlorous acid** is added on in form HO.Cl, forming chlorhydrins.

$$\underset{\text{Ethylene}}{H_2C{:}CH_2} + HO.Cl \longrightarrow \underset{\text{(Ethylene) chlorhydrin}}{HO.CH_2.CH_2Cl.}$$

f. **Hydrogen gas** is seldom directly added on. The hydrogen must be in the nascent form or is made so by the presence of platinum black.

$$H_2C_2 + H_2 = H_2C{:}CH_2 + \text{another } H_2 \longrightarrow C_2H_6.$$

Acetylene — Ethylene — Ethane

$$H_2C{:}CHCH_2OH + H_2 \longrightarrow H_3CCH_2CH_2OH.$$

Allyl alcohol — Propyl alcohol

$$\text{(Benzene ring)} + H_2 \longrightarrow H_2C\langle\;\rangle CH_2 + H_2 \longrightarrow$$

Benzene — Dihydro benzene

$$\text{(CH}_2\text{ CH}_2\text{) } H_2C\langle\;\rangle CH_2 + H_2 \longrightarrow H_2C\langle\;\rangle \text{ (CH}_2\text{ CH}_2\text{, CH}_2\text{ CH}_2\text{).}$$

Tetrahydro benzene — Hexahydrobenzene, Hexamethylene

This, of course, is generally classified as Reduction.

Other addition reactions are considered under other heads —Reduction, Oxidation, etc. Some of these are given by special groups of cpds. in which either the C atoms are doubly linked to other elements, as in aldehydes and ketones (see XIV. 2), or the unsaturation is that of elements other than C, as of N in the amines, amides, cyanides (see XI), or of S in thioethers and mercaptans.

$$Cl_3CHC{:}O + H_2O \longrightarrow Cl_3CHC(OH)_2.$$

Chloral — Chloral hydrate

$$C_2H_5SH \longrightarrow C_2H_5SO_2H \longrightarrow C_2H_5SO_3H.$$

Mercaptan — Sulphinic acid — Sulphonic acid

$$(C_2H_5)_2S \longrightarrow (C_2H_5)_2SBr_2 \text{ or} \longrightarrow (C_2H_5)_2SO \longrightarrow (C_2H_5)_2SO_2.$$

Thioether — Sulphoxide — Sulphone

Addition probably always precedes condensation.

$$\underset{\|\atop O}{CH_3COH} + HOEt \longrightarrow \underset{HO\;\;OEt}{CH_3COH} \longrightarrow H_2O + \underset{|\atop OEt}{CH_3C{:}O}$$

Monoethyl orthoacetate — Ethyl acetate

CONJUGATED BONDS.

Substs. belonging to the class of diolefines show some peculiar addition reactions. Thus a subst. like RCH : CH. CH : CHR might be supposed to add on $2H_2$ or $2Br_2$ at once or to take up Br_2 or H_2 at one of the double linkages forming, *e.g.* RCHBr.-CHBr. CH:CHR, and then RCHBr. CHBr. CHBr. CHBr . R. But the first molecule of Br. attacks both double linkages at once, forming a cpd. RCHBr. CH : CH.CHBrR with a new double linkage. This is the fact on which Thiele has based his views on the existence of a peculiar partial valency, and has suggested for the intermediate linkage the term "conjugated bond." Thus the dotted lines represent the partial valency, the medial ones forming the conjugated bond. On this view benzene has three such bonds, which explains why it does not in general behave as an unsaturated body.

RCH:CH.CH:CHR
Br Br

When a substance contains two unsaturated linkages of different type, different results are produced by the action of reagents which can react with both. Thus in mesityl oxide $(CH_3)_2$ C : CH. CO. CH_3, containing an ordinary C : C link and a carbonyl link, halogen acids are added on as usual at the former. But nascent H from alkaline reagents leaves the C : O group untouched, but opens up the double link, two molecules of the ketone uniting to form a saturated diketone which then eliminates H_2O giving a cyclic cpd.

$$\begin{array}{l} (CH_3)_2C.CH_2COCH_3 \\ \quad\quad | \\ (CH_3)_2C.CH_2COCH_3 \end{array} \longrightarrow \begin{array}{l} (CH_3)_2C.C\,H_2 \\ \quad\quad | \qquad\quad C.CH_3 \\ (CH_3)_2C.C\ COCH_3 \end{array}$$

while Na and moist ether give simply the cpd.

$$(CH_3)_2CH.CH_2CHOH\,CH_3$$

by attacking both double linkages.

CHAPTER IV.

REACTION WITH CUPROUS CHLORIDE.

This is the reaction for *cpds.* having the *terminal group* $C : CH$, but *not* for diolefines having $>C:C:C<$, *nor* for symmetrical disubstituted acetylenes $RC : CR$. It occurs with other unsaturated cpds. In some cases it appears to be addition; in some, however, substitution.

a. In ammoniacal soln., *i.e.* cuprous oxide.

$$\underset{\text{Acetylene}}{HC : CH} + Cu_2O = \underset{\substack{\text{"Cuprosovinylhydroxide."}\\ \text{Addition}}}{CuHC{:}CCu(OH)} \text{ or } \underset{\substack{\text{Cuprous acetylide hydrated.}\\ \text{Replacement}}}{Cu_2C_2,H_2O}.$$

$$\underset{\text{Allylene}}{2CH_3C : CH} + Cu_2O = \underset{\substack{\text{Cuprous allylide}\\ \text{substitution since anhydrous}}}{(CH_3C : C)_2Cu_2} + H_2O.$$

$$\underset{\text{Propiolic ester}}{2HC : C.COOEt} + Cu_2O = Cu_2(C : CCOOEt)_2 + H_2O.$$

Under similar circumstances, these bodies react similarly with silver nitrate.

β. In acid (conc. hydrochloric) soln.

Carbon monoxide forms addition products such as $CO.Cu_2Cl_2$.

Diazo-cpds. form addition products: Sandmeyer's Reaction.

$$\underset{\text{Diazonium chloride}}{\begin{matrix}Ph\\ Cl\end{matrix}\!>\!N : N} + Cu_2Cl_2 \rightarrow \begin{matrix}\begin{matrix}Ph\\ Cl\end{matrix}\!>\!N & : & N\\ | & & |\\ CuCl & & CuCl\end{matrix} \longrightarrow N_2 + \underset{\text{Phenyl chloride.}}{PhCl} + Cu_2Cl_2.$$

$$\text{or } PhN{:}NCl + Cu_2Cl_2 \longrightarrow PhN(CuCl).N\!<\!\begin{matrix}Cl\\ CuCl\end{matrix} \longrightarrow \text{as above.}$$

CHAPTER V.

REPLACEMENT OF HYDROGEN.

This in one form or another is common to *all organic cpds. containing hydrogen.* There are various cases :—

a. **Hydrogen linked to Carbon.**

a. The hydrogen linked to carbon is replaced by halogens (= X)—replacement only.

This is halogenation in the commonest case, the hydrogen attached to carbon forming part of the alkyl, aryl, or alkyl-aryl nucleus of various groups of cpds.

One	two	etc. molecules of halogen X_2 react, producing
mono	di	etc. substituted derivatives, and eliminating
one	two	etc. molecules of halogen hydride, HX.

It may be possible in some cases to carry out this substitution to a certain determinate extent, mono-, di-, etc., substitution, but in general a mixture of derivatives results.

Again, it may be possible to replace H atoms in certain positions, 1, 2, 3, etc., or ortho, meta, para, by attention to certain necessary conditions.

For further substitution, and especially for complete substitution, it may be necessary to carry out the reaction in presence of a third substance—a "*halogen carrier.*" This acts by easily forming a cpd. with the halogen, which cpd. then reacts with the body to be halogenated, supplying halogen to it, then itself recombining with more halogen, giving it up again, and so on.

Such are iodine (forming ICl_3 and ICl), iron (wire, etc.) (to $FeCl_3$ and $FeCl_2$), $SbCl_3$ (to $SbCl_5$), phosphorus or PX_3 (to PX_5), and the aluminium mercury couple (to AlX_3).

CH_4 and Cl_2 give chlormethanes CH_3Cl (Mono-) CH_2Cl_2 (Di-) $CHCl_3$ (Tri-) CCl_4 (Tetra-).

CH_3COOH and Cl_2 give $CH_2ClCOOH$ (Mono-) $CHCl_2COOH$ (Di-) CCl_3COOH (Tri-chloracetic acids)

in mixture more or less according to time and quantities.

$$\begin{array}{c} CH_2COOH \\ | \\ CH_2COOH \end{array} \text{ gives } \begin{array}{c} CHBrCOOH \\ | \\ CH_2COOH \end{array} \text{ and } \begin{array}{c} CHBrCOOH \\ | \\ CHBrCOOH \end{array}$$

Succinic acid — Monobromsuccinic — Dibromsuccinic acids

according to the quantity of Br used.

CH_3CH_2COOH (Propionic acid) gives $CH_3CHBrCOOH$ (α-monobrom) and CH_3CBr_2COOH, ($\alpha\alpha$-dibrompropionic acids)

the halogen going to the same (α) C atom as long as any hydrogen is left, then to the (β) C atom similarly.

C_6H_6 (Benzene) gives C_6H_5Br (Monobrom) then $C_6H_4Br_2$ (Dibrombenzene para (and some ortho))

in presence of iron wire or AlHg couple.

$C_6H_5CH_3$ (Toluene) gives $C_6H_5CH_2Cl$ (Benzyl chloride) $C_6H_5CHCl_2$ (Benzylidene dichloride) $C_6H_5CCl_3$ (Benzotrichloride)

when boiling and in sunlight. At ordinary temperatures in sunlight in presence of a carrier mono-, di-, etc., chlortoluenes:—

$ClC_6H_4CH_3$, $Cl_2C_6H_3CH_3$, etc. are formed.

$$CH_4,\ C_2H_6,\ C_3H_8,\ C_6H_6\ (C_2H_5)_2O,$$

give as end products

$$CCl_4,\ C_2Cl_6,\ C_3Cl_8,\ C_6Cl_6\ (C_2Cl_5)_2O,$$

the formation of these being attended with greatly increasing difficulty.

b. Hydrogen is replaced by halogens with accompanying oxidation.

This is the case with *alcohols.*

$$CH_3CH_2OH \text{ and } Cl_2 \text{ give } CCl_3HC{<}\begin{array}{l} OEt \\ OH \end{array}$$

Ethyl alcohol — Chloral alcoholate

this being the end product after many intermediate products.

In presence of alkali, these compounds are hydrolysed

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + 4I_2 = \underset{\text{Iodal}}{CI_3HCO} + 5HI;$$

$$\text{with } 6KOH \longrightarrow \underset{\text{Formate}}{HCOOK} + 5KI + \underset{\text{Iodoform}}{CHI_3} + 5H_2O.$$

This is sometimes used as a test for ethyl alcohol—best for small quantities.

$\underset{\text{Acetone}}{CH_3COCH_3}$ gives $\underset{\text{Dichloracetone}}{ClCH_2COCH_2Cl}$ when Cl_2 is passed into boiling acetone, but at lower temperatures iodine and alkali act as follows :—

$$\underset{\text{Acetone}}{CH_3COCH_3} + 3I_2 = \underset{\text{Triiodoacetone}}{CH_3COCI_3} + 3HI:$$

$$\text{and} \quad + 4KOH \longrightarrow 3H_2O + 3KI + \underset{\text{Acetate}}{CH_3COOK} + \underset{\text{Iodoform}}{CHI_3}.$$

c. Hydrogen linked to carbon may be replaced by sodium (potassium)—

(i) In *acetylene* and *alkyl acetylenes* of type RC ⫶ CH

$$\underset{\text{Acetylene}}{2HC \vdots CH} + 2Na = \underset{\text{Sodium acetylide}}{2HC \vdots CNa} + H_2,$$

$$\underset{\text{Allylene}}{2CH_3C \vdots CH} + 2Na = \underset{\text{Sodium allylide}}{2CH_3C \vdots CNa} + H_2.$$

The action stops here in this case.

$$2HC \vdots CH + 4Na = \underset{\text{Sodium "carbide"}}{2NaC \vdots CNa} + 2H_2.$$

But diolefines, type RHC:C:CHR, and dialkyl acetylenes, of type RC ⫶ CR, do *not* give this reaction.

(ii) One H atom of a CH_2 or CHR group having CO groups next it—CO.CH_2.CO, as in malonic esters and asymmetric homologues $RHC(COOR')_2$ and in β-ketonic acid esters $RCOCH_2COOR'$ and primary and secondary nitro bodies RCH_2NO_2, $RR'CHNO_2$

is replaceable, unless these be considered as acting in their (HO) or enolic forms RC(OH):CHCOOR′, RHC(NO)OH, RR′C(NO)OH (see below).

$H_2C(COOR)_2$ gives $HNaC(COOR)_2$.
Malonic ester — Sodiomalonic ester

$RHC(COOR')_2$ gives $RNaC(COOR')_2$.
Alkylmalonic ester — Alkylsodiomalonic ester

$RCOCH_2COOR'$ gives $RCOCHNa(COOR')$.
β-ketonic ester — Sodio derivative

$H_2C(COOR)_2$ also gives $Na_2C(COOR)_2$, there being two CO groups.

RCH_2NO_2 gives $RCHNaNO_2$.
Primary nitro — Sodio derivative

$RR'CHNO_2$ gives $RR'CNaNO_2$.
Secondary nitro — Sodio derivative

β. *a.* In some cases, hydrogen attached to other elements than carbon can be replaced by halogen.

Methylamine, CH_3NH_2, gives CH_3NBr_2.
Methyl mercaptan, CH_3SH, gives CCl_3SCl, perchlormethyl mercaptan.

CH_3CONH_2 gives $CH_3CONHBr$ (Hofmann).
Acetamide — Acetmonobromamide

b. Hydrogen linked to other elements may be replaced by sodium (potassium).

(i) In all *OH* and *SH cpds.*, alcohols, phenols, carboxyl and sulphonyl, etc., acids, mercaptans, thioacids, etc.

$2C_2H_5OH + 2Na = 2C_2H_5ONa + H_2$.
Ethyl alcohol — Ethoxide

$2(CH_3)_3C(OH) + 2Na = 2(CH_3)_3CONa + H_2$.
Tertiary butyl alcohol

$2CH_3COOH + 2Na = 2CH_3COONa + H_2$.
Acetic acid — Acetate

$2C_6H_5OH + 2Na = 2C_6H_5ONa + H_2$.
Phenol — Phenate

$$C_6H_4<\begin{matrix}OH\\COOH\end{matrix} + 2Na = C_6H_4<\begin{matrix}ONa\\COONa\end{matrix} + H_2.$$
Salicylate (phenol acid) — "Basic" salt

$$CH_3CHOHCOOH + 2Na = CH_3CHONaCOONa + H_2.$$
Lactic (alcohol acid) — "Basic" salt

$$2C_6H_5SO_3H + 2Na = 2C_6H_5SO_3Na + H_2.$$
Sulphonic acid — Sulphonate

$$2C_6H_5SO_2H + 2Na = 2C_6H_5SO_2Na + H_2.$$
Sulphinic acid — Sulphinate

$$2C_2H_5SH + 2Na = 2C_2H_5SNa + H_2.$$
Mercaptan — Mercaptide

(ii) In the enolic or OH form of β-ketonic acid esters and of primary and secondary nitro bodies and in the pseudo or OH form of amides, primary and secondary—

$$RC(OH){:}CHCOOR' \longrightarrow RC(ONa){:}CHCOOR'.$$
β-ketonic acid ester

$$RHC<\begin{matrix}NO\\OH\end{matrix} \text{ gives } RHC<\begin{matrix}NO\\ONa\end{matrix}$$
Primary nitro body

$$\text{or } RHC\begin{matrix}\diagup N(OH)\\ \quad | \\ \diagdown O\end{matrix} \text{ gives } RHC\begin{matrix}\diagup NONa.\\ \quad | \\ \diagdown O\end{matrix}$$

$$RR'C<\begin{matrix}NO\\OH\end{matrix} \text{ gives } RR'C<\begin{matrix}NO\\ONa,\end{matrix}$$
Secondary nitro body

$$\text{or } \begin{matrix}R\\R'\end{matrix}>C\begin{matrix}\diagup N(OH)\\ \quad | \\ \diagdown O\end{matrix} \text{ gives } \begin{matrix}R\\R'\end{matrix}>C\begin{matrix}\diagup NONa,\\ \quad | \\ \diagdown O\end{matrix}$$

Tertiary nitro bodies give no such reaction.

$$RCONH_2 \longrightarrow RC\leqslant\begin{matrix}OH\\NR\end{matrix} \longrightarrow RC\leqslant\begin{matrix}ONa\\NH\end{matrix} \text{ primary amide.}$$

$$RR'CONH \longrightarrow RC\leqslant\begin{matrix}OH\\NR'\end{matrix} \longrightarrow RC<\begin{matrix}ONa\\NR'\end{matrix} \text{ secondary amide.}$$

Cyclic imides, *e.g.* succinimide, *may* react similarly, but see below.

$$\begin{array}{l} CH_2CO \\ | \\ CH_2CO \end{array} \!\!> NH \longrightarrow \left[\begin{array}{l} CH_2C \\ | \\ CH_2CO \end{array} \!\!> N(OH) \right] \longrightarrow \begin{array}{l} CH_2C \\ | \\ CH_2CO \end{array} \!\!> N(ONa).$$

(iii) In *amino* NH_2 and *imino* NH cpds. and in *imides* of dicarboxy acids, where NH has CO groups on each side of it, cp. above *a. b.* (ii).

$$\underset{\text{Aniline}}{2C_6H_6NH_2} + 2Na = \underset{\text{Anilide}}{2C_6H_5NHNa} + H_2.$$

Two stages theoretically possible, only one practically realisable.

$$\underset{\text{Diphenylamine}}{2(C_6H_5)_2NH} + 2Na = 2(C_6H_5)_2NNa + H_2.$$

This goes more easily than for aniline—the influence of $2C_6H_5$ groups.

$$\underset{\text{Succinimide}}{\begin{array}{l} CH_2CO \\ | \\ CH_2CO \end{array} \!\!> NH} \longrightarrow \underset{\text{Sodium succinimide}}{\begin{array}{l} CH_2CO \\ | \\ CH_2CO \end{array} \!\!> NNa.}$$

$$\underset{\text{Phthalimide}}{C_6H_4 \begin{array}{l} CO \\ CO \end{array} \!\!> NH} \longrightarrow \underset{\text{Sodium phthalimide}}{C_6H_4 \begin{array}{l} CO \\ CO \end{array} \!\!> NNa.}$$

This reaction does not seem to occur at all easily or commonly with fatty amino and imino bodies, though NH_3 itself gives it; but the latter is intermediate in many ways between the similar compounds of the fatty and of the aromatic groups (Basic reactions XI).

CHAPTER VI.

ACTION OF PHOSPHORUS HALOGENIDES.

Phosphorus halogenides cause the replacement of *OH groups* in *alcohols, acids, phenols*, etc., by *halogens*. Halogen hydride (HX) and some phosphorus cpd. is eliminated. So it is a form of condensation (see VII, XIII), and it is considered separately from the cases given there because for these OH cpds. it is sufficiently general to be considered a group reaction. For the previously prepared cpd., there may in general be substituted red phosphorus and halogen (= X) in proper proportions — white phosphorus reacts too violently. Owing to secondary reactions, it fails more or less with polyhydroxy cpds. and with phenols. Phosphorus trichloride (or its generators) is rather apt to form esters of phosphorous acid as well. Using pentahalogenide, the reaction becomes available also for certain oxy-compounds,—*ethers, aldehydes, ketones*—O being replaced by X_2; with separation into two molecules in the case of ethers.

$$\underset{\text{Ethyl alcohol}}{4C_2H_5OH} + PCl_5 = \underset{\text{Ethyl chloride}}{4C_2H_5Cl} + HCl + PO(OH)_3.$$

The yield with phenol is poor owing to the formation of complex phenolic cpds.

$$\underset{\text{Acetic acid}}{3CH_3COOH} + PCl_3 = \underset{\text{Acetyl chloride}}{3CH_3COCl} + P(OH)_3.$$

$$\underset{\text{Benzoic acid}}{PhCOOH} + PCl_5 \longrightarrow \underset{\text{Benzoyl chloride}}{PhCOCl} + HCl + POCl_3.$$

$$\underset{\text{Methyl alcohol}}{3CH_3OH} + P + 3I = \underset{\text{Methyl iodide}}{3CH_3I} + H_3PO_3.$$

$$\underset{\text{Methyl alcohol}}{6CH_3OH} + PCl_3 \longrightarrow \underset{\text{Methyl chloride}}{3CH_3Cl} + \underset{\text{Methyl phosphite}}{P(OCH_3)_3} + 3H_2O.$$

$$(C_2H_5)_2O + PCl_5 = 2C_2H_5Cl + POCl_3.$$
Ether — Ethyl chloride

$$CH_3HCO + PCl_5 = CH_3HCCl_2 + POCl_3.$$
Aldehyde — Alkylidene dichloride

$$PhSO_2OH + PCl_5 = PhSO_2Cl + HCl + POCl_3.$$
Sulphonic acid — Sulphonic chloride

PCl_5 can also react with the pseudo form of acid amides forming imido chlorides.

$RCONH_2$ passes into RC(OH)NH which gives RCClNH and HCl and $POCl_3$.

PCl_5 reacts similarly with oximes.

$$RHCNOH + PCl_5 = RHCNCl + POCl_3 + HCl.$$
Aldoxime — "Nitrogen chloride"

$$RR'CNOH \longrightarrow RR'CNCl.$$
Ketoxime — "Nitrogen chloride

PCl_5 with ketonic acid esters acts as it does with ketones.

$$CH_3COCH_3 + PCl_5 = CH_3CCl_2CH_3 + POCl_3.$$
Acetone — "Acetone chloride"

$$CH_3COCH_2COOEt + PCl_5 = CH_3CCl_2CH_2COOEt + POCl_3.$$
Ethyl acetoacetate — ββ dichlorbutyric acid.

CHAPTER VII.

CONDENSATION.

Condensation may be defined as the reaction between two or more molecules of the same or of different substs., with elimination of one or more molecules of simpler substs., generally of form HX, and often water, acids, or their salts. It may be divided into: (1) Etherification, (2) Alkylation, (3) Esterification, (4) Acylation; and other processes to be considered in XIII and XIV.

1. **Etherification:** forming O-ethers, cpds. in which two (or more) hydrocarbon radicals are united through one (or more) molecules of oxygen, *i.e.* of the types ROR', $R''(OR)_2$, etc.

The most important methods are as follows:—

a. Alkylsulphuric acid or its salts and *alcohols.*

$$\underset{\text{Alkylsulphuric acid}}{C_2H_5SO_4H} + \underset{\text{Alcohol}}{HOC_2H_5} = H_2SO_4 + \underset{\text{Ether, diethyl}}{C_2H_5OC_2H_5}.$$

$$C_2H_5SO_4K + CH_3OH = KHSO_4 + \underset{\text{Ethylmethyl ether}}{C_2H_5OCH_3}.$$

This is the ordinary method, giving simple or mixed ethers.

b. Haloid cpd. and *alkylate* or *arylate.*

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + \underset{\text{Ethylate}}{NaOC_2H_5} = \underset{\text{Simple ether}}{C_2H_5OC_2H_5} + NaI.$$

$$\underset{\text{Methyl iodide}}{CH_3I} + \underset{\text{Ethylate}}{NaOC_2H_5} = \underset{\text{Mixed ether}}{CH_3OC_2H_5} + NaI.$$

$$CH_3I + \underset{\text{Phenate}}{NaOC_6H_5} = \underset{\text{Phenylmethyl ether}}{CH_3OC_6H_5} + NaI.$$

If the sodio-compounds from esters of β-ketonic acids are considered as formed from the enolic, *i.e.* (OH) form of the

ester, then this is a case in point, the new cpd. being an O-ether.

$$CH_3C(ONa):CHCOOEt + EtI = CH_3C(OEt):CHCOOEt + NaI.$$

β-ketonic ester (enolic form) — Ethyl ether (O-ether)

Dimethyl sulphate is often substituted now for methylation instead of methyl iodide. It is used as in the Schotten-Baumann process for Acylation (*q.v.*).

$$\underset{\text{Phenol}}{C_6H_5OH} + \underset{\text{Dimethyl sulphate}}{Me_2SO_4} + NaOH$$
$$= \underset{\text{Anisol}}{C_6H_5OMe} + \underset{\text{Methylsulphate}}{MeSO_4Na} + H_2O.$$

c. Haloid cpds. of various forms and dry *silver* (etc.) *oxide.*

$$\underset{\text{Ethyl iodide}}{2C_2H_5I} + Ag_2O = \underset{\text{Diethyl ether}}{(C_2H_5)_2O} + 2AgI.$$

2. **Alkylation :** forming N-ethers—the replacement of hydrogen attached to N by a hydrocarbon radical.

a. Direct heating with *haloid cpd.*: as for *amines.*

$$NH_3 + RI = \underset{\text{Primary amine}}{NH_2R} + HI.$$

$$NH_2R + R'I = \underset{\text{Secondary amine}}{NHRR'} + HI.$$

$$NH''RR + R''I = \underset{\text{Tertiary amine}}{NRR'R''} + HI.$$

No further reaction like this is possible and the real products are the HI salts of the amines (and of quaternary amine).

$$\underset{\text{Aniline}}{PhNH_2} + EtI = \underset{\text{Ethylaniline}}{PhNHEt} + HI.$$

$$PhNH_2 + 2EtI = \underset{\text{Diethylaniline}}{PhNEt_2} + 2HI.$$

$$\underset{\text{Succinimide}}{\begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix} \!\!>\! NH} + EtI = \underset{\text{Ethylsuccinimide}}{\begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix} \!\!>\! NEt} + HI.$$

b. Silver or *sodium cpd.* and *haloid cpd* of various forms.

$$PhNHNa + PhI = Ph_2NH + NaI.$$

Sodium amide · Phenyl iodide · Diphenylamine

$$\begin{array}{l}CH_2CO\\ |\\ CH_2CO\end{array}\!\!>NAg + RI = \begin{array}{l}CH_2CO\\ |\\ CH_2CO\end{array}\!\!>NR + AgI.$$

Silver succinimide · Alkyl succinimide

In the case of amides, isomeric O- and N-ethers may exist; thus benzamide, $C_6H_5CONH_2$, can give both $C_6H_5C(OEt)(NH)$, O-ether, and $C_6H_5CONHEt$, N-ether. Of course in such cases the original amide may exist in tautomeric (or isomeric) forms.

3. **Esterification:** O-esters.

An ester contains hydrocarbon radicals, one or more, joined by oxygen to acid (or acyl) radicals, one or more, so is of types $RCOOR'$. $R''(COOR)_2$, etc.

The main methods are as follows:—

a. Two or more *molecules, acidic* and *alcoholic* (*i.e.* basic) react, eliminating water under the influence of a "condensing reagent,"—here a dehydrating agent—such as conc. sulphuric acid, zinc chloride, hydrogen chloride gas or its conc. soln., phosphoryl chloride, glacial acetic acid. In the case of the polybasic organic acids, the replacement of the H atoms of the acid is often partial, cpds. called ester-acids resulting.

$$C_2H_5OH + HOAc = C_2H_5OAc + H_2O \text{ (to conc. } H_2SO_4\text{.)}.$$

Alcohol · Acid · Ester

$$CH_3OH + HCl = CH_3Cl + H_2O \text{ (to } ZnCl_2\text{)}.$$

Alcohol · Gas · Ester

$$C_2H_5OH + HOBz + HCl = C_2H_5OBz + HCl \text{ aq}.$$

Benzoic acid · Gas · Benzoate

$$C_2H_4(OH)_2 + 2HOAc = C_2H_4(OAc)_2 + 2H_2O.$$

Glycol · (Glycol) diacetate

$$C_2H_5OH + H_2C_4H_4O_6 = C_2H_5HC_4H_4O_6 + H_2O.$$

Tartaric · Mon-ethyl tartrate (ester acid)

$$C_2H_5HC_4H_4O_6 + C_2H_5OH = (C_2H_5)_2C_4H_4O_6 + H_2O.$$

Diethyl tartrate

$$C_2H_5OH + HHSO_4 = C_2H_5SO_4H + H_2O.$$
Ester-acid, alkyl-sulphuric acid

$$2C_2H_5OH + H_2HPO_4 = (C_2H_5)_2HPO_4 + 2H_2O.$$
Ester acid, dialkylphosphoric acid

b. Ester acid or its salts (*e.g.*, alkylsulphate) heated with dry *metallic salt*.

$$C_2H_5SO_4H + KBr = C_2H_5Br + KHSO_4.$$
Ethylsulphuric acid — Ethyl bromide

$$C_2H_5SO_4H + NaOAc\ (dry) = C_2H_5OAc + NaHSO_4.$$
Ethylsulphuric — Ethyl acetate

If the ester can be identified by its smell, this forms a very convenient test, applied in an obvious manner.

c. Halogen cpd. (aliphatic) distilled with *silver salt*.

$$C_2H_5I + AgOAc = C_2H_5OAc + AgI.$$
Acetate — Ethyl acetate

$$2C_2H_5I + Ag_2SO_4 = (C_2H_5)_2SO_4 + 2AgI.$$
Diethylsulphate

d. Here may be introduced some similar reactions, though the products are not esters, as shown by the way in which they react with alkalis, *e.g.* :—

Aliphatic halides and silver nitrite give *nitro cpds.*, and some nitrous ester. The former behave as quasi acids, giving salts with alkalis.

$$CH_3I + AgNO_2 = CH_3NO_2 + AgI.$$
Methyl iodide — Nitromethane

$$C_2H_4I_2 + 2AgNO_2 = C_2H_4(NO_2)_2 + 2AgI.$$
Ethylene iodide — Dinitroethane

Alkali nitrites in this case give *nitrous esters*, RONO.

Aliphatic halide or *ester acid* or its *salts* with *alkali cyanide* give *alkyl cyanide* or *acid nitrile*. These do not regenerate metallic cyanide, Hydrolysis, see IX.

$$C_2H_5I + KCN = C_2H_5CN + KI.$$
Ethyl iodide — Ethyl cyanide, propionitril

$$EtSO_4K + KCN = C_2H_5CN + K_2SO_4.$$
Alkylsulphate

In this case, silver cyanide produces a mixture of cyanide with isocyanide, RNC, which again is not an ester.

Arylsulphonates fused with KCN give *aryl cyanide*, but the aryl halides do not give Reactions 1. *b* or *c*; 3. *c* or *d*.

4. Acylation.

Here the reaction is so arranged that the eliminated subst. is some other than water, so that the addition of a foreign condensing agent is not so essential and it is more often merely a "neutralising" agent. In a sense the condensing agent is included in the acylating reagent.

The main methods are as follows:—

Acid chloride (etc.) gives *ester* and HCl.

$$\underset{\text{Acid chloride}}{C_2H_5OH + ClCOCH_3} = \underset{\text{Ester}}{C_2H_5OOCCH_3} + HCl. \quad \textit{Acetylation.}$$

In this case the addition of dry sodium acetate is useful.

$$HCl + NaOAc = NaCl + HOAc.$$

$$C_2H_5OH + \underset{\text{Benzoyl chloride}}{ClCOC_6H_5} = \underset{\text{Ethyl benzoate}}{C_2H_5OCOC_6H_5} + HCl. \quad \textit{Benzoylation.}$$

Benzoylation, etc., can be advantageously effected by alternate addition of the acid chloride and *dil.* aq. alkali until the reaction is complete, as shown by the disappearance of smell of the former. This is the **Schotten-Baumann** process.

$$\underset{\text{Phenol}}{C_6H_5OH} + \underset{\text{Benzoyl chloride}}{ClCOC_6H_5} = \underset{\text{Phenyl benzoate}}{C_6H_5OCOC_6H_5} + HCl.$$

$$\text{and } HCl + NaOH = NaCl + H_2O.$$

Acid anhydride gives *ester* and free acid.

$$\underset{\text{Alcohol}}{C_2H_5OH} + \underset{\text{Anhydride}}{(CH_3CO)_2O} = \underset{\text{Ester}}{C_2H_5OAc} + \underset{\text{Acid}}{HOAc}.$$

$$\underset{\text{Glycerol}}{C_3H_5(OH)_3} + \underset{\text{Acetic anhydride}}{3(CH_3CO)_2O} = \underset{\text{"Triacetin"}}{C_3H_5(OAc)_3} + 3HOAc.$$

Here again the addition of dry NaOAc is advantageous.

When hydrogen attached to N and not to O is replaced by an acyl radical, the operation is to a certain extent of the same kind, and the acyl derivative thus formed is an N-ester. Tertiary amines having no replaceable H cannot be acylated.

Acid chlorides give *acyl derivatives.*

$$C_6H_5NH_2 + AcCl = C_6H_5NHAc + HCl.$$
Aniline (primary) — Acetanilide

$$PhNHMe + AcCl = PhNAcMe + HCl.$$
Methylaniline (secdy.) — Methylacetanilide

Two stages theoretically possible for primary amine, one easily realisable. Only one stage possible for secondary amine and realisable.

$$C_6H_5NH_2 + ClCOC_6H_5 + NaOH = C_6H_5NHCOC_6H_5 + NaCl + H_2O.$$
Aniline — Benzoyl chloride — Benzanilide

This is the **Schotten-Baumann** process.

$$COCl_2 + 2H_2NPh = OC(NHPh)_2 + 2HCl.$$
Carbonyl chloride (Acid chloride) — Diphenylurea

Acid anhydride gives *acyl derivative* and free acid.

$$C_6H_5NH_2 + Ac_2O = C_6H_5NHAc + AcOH.$$
Aniline — Acetanilide

Two stages theoretically possible, one stage realisable thus.

$$C_6H_5NHMe + Ac_2O = C_6H_5NAcMe + AcOH.$$
Methylaniline — Methylacetanilide

One stage possible and realisable for secondary amine.

Anhydrides of dicarboxy acids give alternative reactions.

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O + \begin{matrix}H\,HNPh\\H\,HNPh\end{matrix} = C_6H_4<\begin{matrix}CONHPh\\CONHPh\end{matrix} + H_2O.$$
Phthalyl dianilide

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O + H_2NPh = C_6H_4<\begin{matrix}CO\\CO\end{matrix}>NPh + H_2O.$$
Phthalylanilide or phthalanil

$$\underset{\text{Thioanhydride}}{CS_2} + 2H_2NPh = \underset{\text{Thiocarbanilide or diphenyl-thiourea}}{SC(NHPh)_2} + H_2S.$$

Boil these with alcohol : H_2S is eliminated.

By reaction based on the above action of acid anhydride, the number of (HO) groups in a hydroxy cpd., or of NH_2 or NH groups in an amine—both of known molecular weight—can be determined. Thus, using acetic anhydride, the liberated acetic acid is a measure of the number of OH, NH_2 or NH groups, and is determined by titrating the free acid in mixture. In benzoylation, the number of benzoyl groups, Bz (= PhCO) added is determined by a combustion of the derivative, the composition of which is then compared with that of the original substance.

CHAPTER VIII.

IONISATION.

i. Ionisation may be defined as the change whereby on soln. the positive and negative parts of metallic salts, and generally the basic and acidic parts of any substance become free and independent of one another, so that each can show its own reactions unhindered by the other. These parts are called ions. In the ordinary solns. used in analysis this ionisation is by no means complete, but it becomes so progressively, *i.e.* all, or nearly all, of the molecules pass through the ionic state, as the ions already present are used up by removal from soln., as by precipitation or evolution as gas up to a limit which represents the incompleteness of the reaction (precipitation, gas evolution, etc.). The value of the particular reaction as a quantitative one depends on the smallness of this limit.

Thus the precipitations of silver as silver chloride and of barium as barium sulphate are very complete under conditions—the presence of dil. acids, HNO_3 and HCl respectively, while mercury present as cyanide is not ppd. at all by KOH.

This ionisation is proved and measured by certain physical properties.

Acids contain the *H ion, alkalis* (bases), the *(OH) ion*, each recognised by its action on certain organic coloured substs.—indicators.

The ionising solvent is water, but ionisation may occur also in alcohol, acetone, pyridine, etc., solns.

In general, ionisation is very incomplete among organic bodies, except among salts of alkali metals.

One obvious difference between salts and esters is that the latter are not ionised in aq. soln. sufficiently to give the ion reactions for the acid or basic parts. Thus ethyl acetate does not react with aq. $FeCl_3$, nor indeed ethyl bromide completely with $AgNO_3$, both in alcoholic soln.

ii. **Hydrolysis of salts.** The observation that many salts—

(*a*) Of inorganic bases with organic acids are alkaline in reaction,

(*b*) Of mineral acids with organic bases are acid in reaction:

must be explained by a hydrolytic action of the solvent water—acting as H,OH, thus setting free—

(*a*) alkali } well ionised, { OH } ions } showing the action
(*b*) mineral acid } giving { H } ions } with indicators,

and (*a*) organic acid only very slightly ionised, not showing reaction with indicators, and

(*b*) organic base not forming the hydroxide corresponding to alkali, and not reacting with indicators.

$$C_{17}H_{35}COONa + H.OH = C_{17}H_{35}COOH + NaOH$$

Sodium stearate — Stearic acid not ionised, neutral to indicators — Well ionised, alkaline to indicators

$$C_6H_5NH_3Cl + H.OH = C_6H_5NH_3OH + HCl.$$

Phenylammonium chloride — Passing into — Well ionised acid to indicators

$$C_6H_5NH_2 + H_2O$$

Aniline, neutral to indicators

CHAPTER IX.

HYDROLYSIS.

This is the converse of condensation, consisting of hydration and decomposition into two or more substs. which may react further as acidic or basic, with the hydrolysing reagent, either basic or acidic. The reaction occurs in the following groups of cpds.:—

a. Esters of carboxylic and sulphonic acids: O-esters, from hydroxy derivatives: N-esters, including; amides from NH_3, hydrazides from N_2H_4, and acylamines and acyl-hydrazides from substituted ammonias and hydrazides (*e.g.* $PhNHNH_2$).

β. Ester-acids: *e.g.* alkylsulphates, etc.; "acid" esters, *e.g.* COOEtCOOH; amic acids and their esters, *e.g.* $CONH_2COOH$, etc., and salts of all these.

γ. Substs. in which halogens have replaced hydrogen, except the simple monosubstituted aromatic derivatives.

δ. Ethers: O-ethers, including the biose, etc., sugars; N-ethers, the secondary and tertiary amines and hydrazines; alkylates of metals, arylates (*e.g.* phenates).

ε. Acid halogenides, anhydrides and nitriles.

The following are the reagents most commonly used:—

a. **Water,** especially at high temperatures and pressures ("sealed tube").

a. These give free acid; and free alcohol, NH_3, N_2H_4 or their alkyl or aryl derivatives.

$$\underset{\text{Methyl oxalate}}{\begin{matrix}COOMe\\COOMe\end{matrix}} + H_2O = \underset{\text{Oxalic acid}}{\begin{matrix}COOH\\COOH\end{matrix}} + \underset{\text{Alcohol}}{2MeOH}.$$

This reaction at ordinary temperatures goes in general rather slowly, but some esters (as the one above) are hydrolysed sufficiently to react acid in aq. soln.

δ. O-ethers are *very* slowly hydrolysed by water into alcohols. Alkylates of metals give alcohol and hydroxide of metal (alkali).

$$\underset{\text{Ethylate}}{EtONa} + H_2O = \underset{\text{Alcohol}}{EtOH} + NaOH.$$

$$\underset{\text{Ethylate}}{Ca(OEt)_2} + 2H_2O = \underset{\text{Alcohol}}{2EtOH} + Ca(OH)_2.$$

ε. Acid halogenides give organic and halogen acids, often violently.

$$\underset{\text{Acid (acetyl) chloride}}{CH_3COCl} + H_2O = \underset{\text{Acid (acetic)}}{CH_3COOH} + HCl.$$

$$\underset{\text{Benzoyl chloride}}{C_6H_5COCl} + H_2O = \underset{\text{Benzoic acid}}{C_6H_5COOH} + HCl.$$

Acid anhydrides give organic acids only, and less violently.

$$\underset{\text{Acetic anhydride}}{\begin{matrix} CH_3CO \\ CH_3CO \end{matrix}>O} + H_2O = \underset{\text{Acetic acid, 2 mols.}}{\begin{matrix} CH_3COOH \\ CH_3COOH. \end{matrix}}$$

$$\underset{\text{Succinic anhydride}}{\begin{matrix} CH_2CO \\ CH_2CO \end{matrix}>O} + H_2O = \underset{\text{Succinic acid}}{\begin{matrix} CH_2COOH \\ CH_2COOH. \end{matrix}}$$

b. **Alkalis,** aq. or alcoholic, dil.: potash or soda, baryta or lime water, milk of magnesia: also lead or silver hydroxides or the oxide with water.

This is the most generally useful method.

a. These give salt of organic acid, sol. or insol.; and free alcohol, NH_3, N_2H_4 or their derivatives.

$$\underset{\text{Ester (formate)}}{HCOOC_2H_5} + KOH = \underset{\text{Salt}}{HCOOK} + \underset{\text{Alcohol}}{C_2H_5OH}.$$

$$\underset{\text{Amide (acet.)}}{CH_3CONH_2} + KOH = \underset{\text{Acetate}}{CH_3COOK} + NH_3$$

$$\underset{\text{Acylamine ; acetanilide}}{C_6H_5NHAc} + KOH = \underset{\text{Amine ; aniline}}{C_6H_5NH_2} + \underset{\text{Salt}}{KOAc}$$

$$C_6H_5NHNHAc + NaOH = C_6H_5NHNH_2 + NaOAc$$

Acylhydrazide acetphenylhydrazine; Hydrazine phenyl hydrazine; Salt

$$2C_3H_5(C_{17}H_{33}O_2)_3 + 3PbO + 3H_2O =$$

Triolein (in oils); Litharge

$$2C_3H_5(OH)_3 + 3Pb(C_{17}H_{33}O_2)_2.$$

Glycerol; Lead oleate (insol.)

β. These give salt of original acid; and alcohol or NH_3, etc.

$$EtSO_4K + KOH = EtOH + K_2SO_4.$$

Alkylsulphate; Alcohol; Salt

$$\begin{matrix} CONH_2 \\ COOEt \end{matrix} + 2KOH = \begin{matrix} COOK \\ COOK \end{matrix} + EtOH + NH_3.$$

Amic acid (ester) Oxamic; Oxalate

γ. These give corresponding (HO) cpd. and halogenide.

$$C_2H_5I + AgOH = C_2H_5OH + AgI.$$

Halogen ester; Moist oxide; Alcohol; (insol.)

$$C_2H_4Br_2 + 2KOH = C_2H_4(OH)_2 + 2KBr.$$

Ethylene dibromide; Glycol

$$ClCH_2COOH + 2KOH = HOCH_2COOK + KCl + H_2O.$$

Chloro-acid; chloracetic; Hydroxyacid; glycollate

Esters of such acids give alcohol in addition, of course.

Neither C_6H_5X nor $C_6H_4X_2$ ($X =$ halogen) are so decomposed, but $ClC_6H_4NO_2$, chlornitrobenzene, gives $KOC_6H_4NO_2$, nitrophenate, and KCl.

δ. Ethers are *not* hydrolysed by alkalis.

ε. Acid chlorides and anhydrides give mixed salts; nitriles give salt of organic acid, and NH_3.

$$CH_3COCl + 2KOH = CH_3COOK + KCl + H_2O.$$

Acetyl chloride; Acetate

$$(CH_3CO)_2O + 2KOH = 2CH_3COOK + 2H_2O.$$

Acetic anhydride; Acetate

$$\underset{\text{Nitrile (aceto-) Methyl cyanide}}{CH_3CN} + KOH + H_2O = \underset{\text{Acetate}}{CH_3COOK} + NH_3.$$

$$\underset{\text{Nitrile (benzo-) phenyl cyanide}}{C_6H_5CN} + KOH + H_2O = \underset{\text{Benzoate}}{C_6H_5COOK} + NH_3.$$

Isocyanides are *not* hydrolysed by alkalis.

Tri-chloraldehydes (and chlorketones) are hydrolysed by cold dilute alkalis thus:—

$$\underset{\text{Chloral}}{Cl_3CHCO} + KOH = \underset{\text{Chloroform}}{CCl_3H} + \underset{\text{Formate}}{HCOOK}$$

c. **Acids,** generally hydrochloric or sulphuric, and in varying concentration but most commonly "dilute."

α. O-esters give the same products as with water, only very much more rapidly, the acid acting as accelerator.

N-esters give free acid and salt of basic substance.

$$\underset{\text{Amide; benzamide}}{C_6H_5CONH_2} + HCl + H_2O = \underset{\text{Benzoic acid}}{C_6H_5COOH} + NH_4Cl.$$

$$\underset{\text{Acylamine; benzanilide}}{C_6H_5CONHC_6H_5} + HCl + H_2O = \underset{\text{Benzoic acid}}{C_6H_5COOH} + \underset{\text{Aniline hydrochloride}}{C_6H_5NH_3Cl}.$$

β. Ester-acids give free acid and alcohol, their salts give salt and alcohol. Acid esters and their salts behave similarly.

$$\underset{\text{Ester-acid (salt)}}{EtSO_4K} + H_2O = \underset{\text{Alcohol}}{EtOH} + KHSO_4.$$

γ. Halogen substituted cpds. are not readily hydrolysed thus.

δ. Ethers. O-ethers give alcohols rather slowly, but the biose, etc., sugars and aldehyde and ketone ethers go fairly easily. N-ethers require concentrated acids, see *d*.

$$\underset{\text{Biose sugar Sucrose}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Monose sugars: Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Biose sugar Lactose}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Monose sugars: Glucose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{C_6H_{12}O_6}.$$

$$\underset{\text{Aldehyde ether Acetal}}{CH_3HC(OEt)_2} + H_2O = \underset{\text{Aldehyde}}{CH_3HCO} + \underset{\text{Alcohol}}{2EtOH}.$$

ε. Nitriles, *i.e.* alkyl cyanides, give free acid and ammon. salt.

$$\underset{\text{Methyl cyanide, Acetonitrile}}{CH_3CN} + 2H_2O + HCl = \underset{\text{Acetic acid}}{CH_3COOH} + NH_4Cl.$$

Alkyl isocyanides with conc. HCl give formic acid and amine-HCl.

$$\underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 2H_2O + HCl = \underset{\text{Aniline hydrochloride}}{C_6H_5NH_3Cl} + HCOOH.$$

$$\underset{\text{Ethyl isocyanide}}{C_2H_5NC} + 2H_2O + HCl = \underset{\text{Ethylamine hydrochloride}}{C_2H_5NH_3Cl} + HCOOH.$$

d. **Hydriodic acid,** fuming, is applied for the hydrolysis of O-ethers and N-ethers, the alkyl groups being split off as alkyl iodides—Zeisel's method.

$$\underset{\text{Ethyl ether}}{C_2H_5OC_2H_5} + 2HI = \underset{\text{Ethyl iodide}}{2C_2H_5I} + H_2O.$$

$$\underset{\text{Methylaniline}}{C_6H_5NHCH_3} + 2HI = \underset{\text{Methyl iodide}}{CH_3I} + \underset{\text{Aniline hydriodide}}{C_6H_5NH_3I}.$$

$$\underset{\text{Guaiacol}}{C_6H_4<{OH^{(1)} \atop OCH_3^{(2)}}} + HI = \underset{\text{Catechol}}{C_6H_4<{OH^{(1)} \atop OH^{(2)}}} + CH_3I$$

$$\underset{\text{Dimethylaniline}}{C_6H_5N(CH_3)_2} + 3HI = 2CH_3I + C_6H_5NH_3I.$$

This is used as a means of determining the number of oxy-alkyl groups in O-ethers or alkyl groups in N-ethers, the volatile alkyl iodide being distilled off into alcoholic $AgNO_3$ and the ppd. AgI weighed. In the case of N-ethers, the primary amine remains behind as HI salt.

e. **Potash Fusion.**—A strenuous form of hydrolysis, necessary for certain very stable ester-acids and their salts, *e.g.* sulphonates, converted into HO-bodies.

$$\underset{\text{Phenylsulphonate}}{PhSO_2OK} + 2KOH = \underset{\text{Phenate}}{PhOK} + K_2SO_3 + H_2O.$$

(Phenol set free by acidifying.)

$$\underset{\text{Benzene disulphonate}}{C_6H_4(SO_3K)_2} \longrightarrow \underset{\text{Dihydroxybenzene}}{C_6H_4(OH)_2} + K_2SO_3$$

$$H_2NC_6H_4SO_3H + KOH \longrightarrow H_2NC_6H_5 + KHSO_4.$$
Aniline sulphonic acid — Aniline — Sulphate

$$not\ H_2NC_6H_4OK + KHSO_3$$
Aminophenate — Sulphite

Sulphanilic acid is evidently irregular.

$$C_2H_5SO_2OC_2H_5 + KOH = C_2H_5OH + C_2H_5SO_3K.$$
Unsym. diethylsulphite — First mol. — Ethane sulphonate

By ordinary hydrolysis.

$$C_2H_5SO_3K + KOH = C_2H_5OH + K_2SO_3.$$
Ethane sulphonate — Second mol.

By potash fusion only.

Thus the KOH fusion eliminates SO_2. It can also remove CO_2.

$$C_6H_5COOK + KOH = C_6H_5H + K_2CO_3 + H_2O.$$
Benzoate — Benzene

$$C_6H_4(COOH)_2 + 4KOH = C_6H_6 + 2K_2CO_3 + 2H_2O.$$
Phthalic acid — Benzene

Soda Lime Fusion is quite similar in effect to (*e*), but is a more convenient reagent for referring a carboxyl cpd. (*i.e.*, acid or its salts) to the parent body.

$$CH_3COONa + NaOH = CH_4 + CO_3Na_2.$$
Acetate — Hydrocarbon

$$C_2O_4Na_2 + 2NaOH = H_2 + 2CO_3Na_2.$$
Oxalate

$$HOC_6H_4COONa + NaOH = C_6H_5OH + CO_3Na_2.$$
Hydroxybenzoate (salicylate) — Hydroxybenzene (phenol)

$$ClC_6H_4COONa + NaOH = ClC_6H_5 + CO_3Na_2.$$
Chlorbenzoate — Chlorbenzene

$$NO_2C_6H_4COONa + NaOH = NO_2C_6H_5 + CO_3Na_2.$$
Nitrobenzoate — Nitrobenzene

$$C_6H_4<^{SO_3Na}_{CO_2Na} + 2NaOH = C_6H_5OH + Na_2SO_3 + Na_2CO_3.$$
Sulphobenzoate — Phenol

f. Sulphonic acids are hydrolysed by **superheated steam** in presence of conc. acids—sulphuric—so as to liberate the original substance sulphonated.

$$\underset{\text{Sulphonic acid}}{C_6H_5SO_3H} + H_2O = \underset{\text{Benzene}}{C_6H_5H} + H_2SO_4.$$

$$\underset{\text{Chlorbenzene sulphonic acid}}{C_6H_4{<}{}^{SO_3H}_{Cl}} + H_2O = \underset{\text{Chlorbenzene}}{C_6H_5Cl} + H_2SO_4.$$

CHAPTER X.

ELIMINATION.

This reaction differs from condensation in that the part eliminated comes in general wholly from one molecule, the residues in some cases uniting (*c*).

There are various cases :—

a. Water is eliminated : **dehydration.**

α. By direct heating alone.

Ammonium salts of *monocarboxy acids* give *amides*.

$$\underset{\text{Ammonium acetate}}{CH_3COONH_4} = \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O.$$

Hydrogen ammonium salts of *dicarboxy acids* give *amic acids*.

$$\underset{\text{Ammonium hydrogen succinate}}{\begin{matrix} CH_2COONH_4 \\ | \\ CH_2COOH \end{matrix}} = \underset{\text{Succinamic acid}}{\begin{matrix} CH_2CONH_2 \\ | \\ CH_2COOH \end{matrix}} + H_2O.$$

β-hydroxy acids and their *aldehydes* give *unsaturated acids* and *aldehydes*.

$$\underset{\text{Hydracrylic}}{CH_2OH.CH_2COOH} \longrightarrow \underset{\text{Acrylic}}{CH_2 : CHCOOH.}$$

$$\underset{\beta\text{-hydroxy HO-butyric}}{CH_3CHOH.CH_2COOH} \longrightarrow \underset{\text{Crotonic}}{CH_3CH : CHCOOH.}$$

$$\underset{\beta\text{-HO-butyraldehyde}}{CH_3CHOH.CH_2HCO} \longrightarrow \underset{\text{Crotonaldehyde}}{CH_3CH : CH.HCO.}$$

This is the conclusion of what is known as the "Aldol Condensation."

α-Hydroxy acids give various *anhydrides* formed from *two molecules.* This is a case of condensation; some of the anhydrides are like ethers, some like esters, some like both, according to the original position of the derived H.OH groups.

$$\begin{matrix} CH_3CHOHCOOH \\ HOOCCHOHCH_3 \end{matrix} \longrightarrow O<\begin{matrix} CH(CH_3)CO \\ COCH(CH_3) \end{matrix}>O.$$

Lactic acid — Lactide, double ester

$$\begin{matrix} HOCH_2COOH \\ HOOCCH_2OH \end{matrix} \longrightarrow O<\begin{matrix} CH_2CO \\ COCH_2 \end{matrix}>O.$$

Glycollic acid — Ether-ester anhydride

δ- and γ- hydroxy-acids give cyclic anhydrides called *lactones,* one mol. from one mol. of acid. This happens often at the ordinary temperature.

$$\begin{matrix} CH_2CH_2OH \\ | \\ CH_2COOH \end{matrix} \longrightarrow \begin{matrix} CH_2CH_2 \\ | \\ CH_2CO \end{matrix}>O.$$

γ- hydroxy-butyric — Butyrolactone

Dicarboxy aliphatic acids give *cyclic anhydrides* except when the carboxy groups are separated by four or more CH_2 groups.

$$\begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix} \longrightarrow \begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix}>O.$$

Succinic acid — Succinic anhydride

$$\begin{matrix} CH_2CH_2COOH \\ | \\ CH_2CH_2COOH \end{matrix}$$ Volatilises unchanged under diminished pressure.

Adipic acid

Aromatic ortho-dicarboxy acids also give *cyclic anhydrides.*

$$C_6H_4\begin{matrix} COOH \\ COOH \end{matrix} \longrightarrow C_6H_4\begin{matrix} CO \\ CO \end{matrix}>O.$$

Phthalic acid — Phthalic anhydride

The meta- and para- acids are distinguished by not forming anhydrides.

Unsaturated olefine dicarboxy acids in which the *COOH groups* are on the *same side*, *i.e.* the cis form, behave similarly.

$$\begin{matrix} CH.COOH \\ \| \\ CH.COOH \end{matrix} \longrightarrow \begin{matrix} CH.CO \\ \| \\ CH.CO \end{matrix} O.$$

Maleic acid — Maleic anhydride

$$\begin{matrix} CH_3.C.COOH \\ \| \\ H.\ C.COOH \end{matrix} \longrightarrow \begin{matrix} CH_3.C.CO \\ \| \\ H.C.CO \end{matrix} O.$$

Citraconic — Anhydride

β. Heating with dehydrating agents, P_2O_5, $POCl_3$, $ZnCl_2$, conc. H_2SO_4.

Amides give *nitriles*, *i.e.* cyanides.

$$CH_3CONH_2 + P_2O_5 = CH_3CN + H_2P_2O_6.$$

Acetamide — Acetonitrile

$$C_6H_5CONH_2 + P_2O_5 = C_6H_5CN + H_2P_2O_6.$$

Benzamide — Benzonitrile

$$\begin{matrix} CONH_2 \\ CONH_2 \end{matrix} + 2P_2O_5 = \begin{matrix} CN \\ \||| \\ CN \end{matrix} + 2H_2P_2O_6$$

Oxamide — Oxalonitrile

b. *Acids* in the form HX (X often halogen) *are removed by boiling with alcoholic potash or soda,* leaving unsaturated body.

Removal of one HX leaves olefine cpd.

$$CH_3CH_2Br + KOH = C_2H_4 + KBr + H_2O.$$

Ethyl bromide — in alc. — Ethylene

$$PhCH_2CH_2Br \longrightarrow PhCH{:}CH_2.$$

Bromethyl benzene — Styrolene

$$CH_3CHBrCOOH \longrightarrow CH_2{:}CHCOOH$$

α-Brompropionic acid — Acrylic acid

Removal of two HX groups in stages (or together) *leaves acetylene cpd.*

CH_2BrCH_2Br + KOH, alcoholic.
Ethylene dibromide $= KBr + H_2O + CH_2{:}CHBr$ and then $CH \vdots CH$.
Vinyl bromide — Acetylene

$CH_2BrCHBrCOOH \longrightarrow CH_2{:}CHBrCOOH \longrightarrow HC \vdots C.COOH$.
$\alpha\beta$-Dibrompropionic acid — Bromacrylic acid — Propiolic acid

Similarly

$CH_2Br.CHBr.CH_2.CH_2CHBr.CH_2Br \rightarrow HC \vdots C.CH_2.CH_2.C \vdots CH$.
Diallyltetrabromide — Dipropargyl: an isomer of benzene

c. **Elimination of Halogen by the action of Metals,** *e.g.* ppd. or molecular silver, sodium or rarely potassium: subst. mixed with dry ether.

Aliphatic hydrocarbons from haloid esters. Two or more, similar or dissimilar. Wurtz's Reaction.

$C_2H_5I + CH_3I + 2Na = CH_3CH_2CH_3 + 2NaI$.
Ethyl iodide — Methyl iodide — Propane

$C_2H_4Br_2 + 2CH_3I + 4Na = CH_3CH_2CH_2CH_3 + 2NaBr + 2NaI$.
Ethylene dibromide — Methyl iodide — n-Butane

$2C_2H_5I + 2Na = C_2H_5C_2H_5 + 2NaI$ n-Butane again.

Similarly *carbocyclic dicarboxylic esters* from disodiomalonic esters and dihaloid cpds.

$$\begin{matrix}EtO_2C\\EtO_2C\end{matrix}>CNa_2 + \begin{matrix}BrCH_2\\BrCH_2\end{matrix} = (EtO_2C)_2C\left<\begin{matrix}CH_2\\|\\CH_2\end{matrix}\right.$$
Trimethylene dicarboxylic ester.

Similarly *dicarboxy acids* from *halosubstituted acids.*

$2BrCH_2COOH + 2Ag = (CH_2COOH)_2 + 2AgBr$.
Bromacetic acid — Succinic acid

Also *aromatic hydrocarbons from halogen cpds.* Fittig's Reaction.

$C_6H_5Br + C_2H_5Br + 2Na = C_6H_5C_2H_5 + 2NaBr$.
Phenyl bromide — Ethyl bromide — Ethyl benzene

$C_6H_5CH_2Br + C_6H_5Br + 2Na = C_6H_5CH_2C_6H_5 + 2NaBr$.
Benzyl bromide — Phenyl bromide — Diphenylmethane

Some other metals, *e.g.* zinc, magnesium, react so as to produce also cpds. of the metal and hydrocarbon radical.

$$2EtI + 2Zn = 2ZnEtI \text{ and } 2ZnEtI = ZnEt_2 + ZnI_2 \quad \text{at a higher temperature.}$$

Alkyl iodide — Zinc ethiodide — Zinc ethyl

From this zinc alkyl other metallo-organic cpds. are obtained by exchange.

$$2ZnEt_2 + SnCl_4 = SnEt_4 + 2ZnCl_2.$$
$$3ZnMe_2 + 2AlCl_3 = 2AlMe_3 + 3ZnCl_2.$$

In presence of absolute dry ether (or dimethylaniline) magnesium reacts as follows, forming oxonium (or ammonium) cpds. This is *Grignard's Reagent.*

$$Mg + EtI + Et_2O = {}^{Et}_{Et}{>}O{<}^{Et}_{MgI}.$$

$$Mg + EtI + PhNMe_2 = \begin{matrix} Ph \\ Me- \\ Me/ \end{matrix} N{<}^{Et}_{MgI}.$$

These cpds. are used in the synthesis of many cpds., of very varied kinds.

d. **Elimination of carbon dioxide,** by heating alone, from *dicarboxy acids* with both *COOH groups on the same C atom* — malonic acid and its homologues.

$$\underset{\text{Malonic acid}}{H_2C(COOH)_2} = \underset{\text{Acetic acid}}{CH_3COOH} + CO_2.$$

$$\underset{\text{Methylmalonic}}{CH_3CH(COOH)_2} = \underset{\text{Propionic}}{CH_3CH_2COOH} + CO_2.$$

Elimination of CO_2 or of SO_2 by heating with soda lime or with KOH (IX. *f.*) may be considered as a case in point.

e. **Elimination of ammonia** in form $H.NH_2$ by heating *diamides* in HCl gas, giving *cyclic imides.*

$$\underset{\text{Succinamide}}{\begin{matrix} CH_2CONH_2 \\ | \\ CH_2CONH_2 \end{matrix}} + HCl = \underset{\text{Succinimide}}{\begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix}{>}NH} + NH_4Cl.$$

Certain *diamines* treated similarly give *cyclic bases.*

$$\begin{array}{l} CH_2CH_2NH_2 \\ | \\ CH_2CH_2NH_2 \end{array} + HCl = \begin{array}{l} CH_2CH_2 \\ | \\ CH_2CH_2 \end{array}\!\!\!>NH + NH_4Cl.$$

Tetramethylene diamine — Pyrrolidine

f. Aromatic diazo cpds. Diazonium salts eliminate **nitrogen** as follows :—

On heating with water (sulphates best), producing *hydroxy cpds.*

$$\underset{\text{Benzene diazon. sulphate}}{C_6H_5N(SO_4H) : N} + H_2O = \underset{\text{Phenol}}{C_6H_5OH} + H_2SO_4 + N_2.$$

On boiling (sulphates best) with alcohol; giving *hydrocarbon* and aldehyde.

$$C_6H_5N(SO_4H) : N + C_2H_5OH$$
$$= \underset{\text{Benzene}}{C_6H_5H} + \underset{\text{Acetaldehyde}}{CH_3HCO} + N_2 + H_2SO_4.$$

On boiling (sulphates) with potassium, etc., halides: giving *aryl halide.*

$$C_6H_5N(SO_4H) : N + KBr = \underset{\text{Brombenzene}}{C_6H_5Br} + N_2 + KHSO_4.$$

This last goes much more easily using Sandmeyer's method, *i.e.* boiling with cuprous halide or (Gattermann) with copper powder and halogen acid or its salts (K. *e.g.*).

$$\underset{\text{Diazon. chloride}}{PhNCl : N} \longrightarrow PhCl + N_2.$$

$$2PhNCl : N + Cu_2Br_2 = 2PhBr + Cu_2Cl_2 + 2N_2.$$

Similarly cuprous cyanide (or Cu and KCN) gives *nitriles.*

$$2PhNCl : N + \underset{\text{In KCN}}{Cu_2(CN)_2} = \underset{\text{Phenyl cyanide or benzonitril}}{2PhCN} + 2N_2 + Cu_2Cl_2.$$

There are a number of other similar changes.

CHAPTER XI.

BASIC REACTIONS.

These are found chiefly among nitrogen cpds.—simple and complex substituted ammonias. The acid is added on in virtue of the power of the originally trivalent N atoms to become pentavalent. The bases are therefore mono-, di-, etc., acid according to the number of trivalent N atoms which can (or may in a given case) become pentavalent; thus a base need not manifest its full acidity, *e.g.* N_2H_4, hydrazine, forms $N_2H_4.HCl$ and $N_2H_4.2HCl$ as well as $N_2H_4.H_2SO_4$, and similarly the phenylene diamines, $C_6H_4(NH_2)_2$ can form $C_6H_4(NH_2)_2.HCl$ and $C_6H_4(NH_3)_2Cl_2$, while phenylhydrazine can form only $C_6H_5NHNH_3Cl$, owing probably to the action of the "acidic" group, C_6H_5, next the other N atom. But a nitrogen atom may be nonbasic because already pentavalent. This is the case in strychnine, which, though a diamine, is only monoacid, *e.g.* $C_{21}H_{22}N_2O_2.HNO_3$, while quinine, also a diamine, can form $C_{20}H_{24}N_2O_2.H_2SO_4$ and $C_{20}H_{24}N_2O_2.HCl$. Urea is monoacid, *e.g.* $NH_2CONH_3NO_3$, probably because of the "acidic" group, CO, next one N atom.

The various reactions are of the following types:—

a. **Combination with inorganic acids.**

α. Forming soluble salts.

This is exactly similar to the case for NH_3. The reaction is, in certain cases ("stronger" bases), so exactly quantitative, that it can be carried out by a titration with the acid, methyl orange as indicator, the salt being ionised more or less completely, but not hydrolysed to an appreciable extent (see VIII ii.). This reaction may be applied in the estimation of the base or in the determination of its "equivalent."

It is seldom possible with organic acids, owing to hydrolysis of the salt by water setting in before neutralisation is complete.

$C_2H_5NH_2 + HCl = C_2H_5NH_3Cl.$
Ethylamine (base, alkaline) — Ethylammonium chloride (salt, neutral)

$2C_6H_5NH_2 + H_2SO_4 = (C_6H_5NH_3)_2SO_4.$
Aniline (weak base) — Phenylammonium sulphate (salt, acid)

$C_{21}H_{22}N_2O_2 + HNO_3 = C_{21}H_{23}N_2O_2NO_3.$
Base, strychnine, "dissolves" in acid

$PhNH_2 + HOAc (= PhNH_3OAc) = PhNHAc + H_2O.$
Aniline — Acetic — Unreal — Acetanilide by condensation

When, as in this case, an attempt is made to obtain a real salt, then water is eliminated, an acyl derivative being formed by condensation (*q.v.*), VII 4.

β. Forming salts, sufficiently insol. in water, in alcohol or in the acid added, to be ppd.

The base may be "estimated" or its equivalent found in this case. Suitable cases are chloroplatinates or chloraurates—the ppd. salt being either weighed as such or the residual Pt or Au remaining after ignition of a known weight determined.

$H_2NCONH_2 + HNO_3 = H_2NCONH_3NO_3.$
Urea — Urea nitrate, insol. HNO_3.

$C_{20}H_{16}N_4 + HNO_3 = C_{20}H_{17}N_4NO_3.$
"Nitron" — Nitron nitrate, most insol. nitrate known

$2C_{21}H_{22}N_2O_2 + H_2PtCl_6 = (C_{21}H_{23}N_2O_2)_2PtCl_6$
Strychnine — S. chloroplatinate

$C_{20}H_{26}N_2O_2SO_4 + K_2HgI_4 = C_{20}H_{26}N_2O_2HgI_4 + K_2SO_4.$
Quinine sulphate — Mayer's reagent — Quinine mercuriodide

b. **Displacement of the organic base by an inorganic base,** as NH_3 is by NaOH or $Ca(OH)_2$.

In many cases this may be applied as an indirect estimation

of the base (or a determination of its equivalent) by titrating the acid present, using an indicator such as phenolphthalein, to which the base itself is neutral.

a. Volatile bases are expelled by boiling or distilling in steam.

$$\underset{\text{Ethylammonium chloride}}{C_2H_5NH_3Cl} + NaOH = \underset{\text{Ethylamine}}{C_2H_5NH_2} + NaCl + H_2O.$$

$$\underset{\text{"Aniline sulphate"}}{(C_6H_5NH_3)_2SO_4} + 2NaOH = \underset{\text{Aniline (neutral to phenolphthalein)}}{2C_6H_5NH_2} + Na_2SO_4 + 2H_2O.$$

β. Insol. bases are ppd. and filtered off, to be weighed if sufficiently insol.

$$\underset{\text{Strychnine nitrate}}{C_{21}H_{23}N_2O_2NO_3} + NaOH = \underset{\text{Strychnine, pp.}}{C_{21}H_{22}N_2O_2} + NaNO_3 + H_2O.$$

c. **Removal of weaker inorganic bases from their acids.**

Generally the inorganic base is ppd. as a hydroxide, this suggesting that the organic base must exist in soln. as a hydroxide, more or less completely ionised.

$$AlCl_3 + \underset{\text{Ethylamine}}{3EtNH_2} + 3H_2O = \underset{\text{pp.}}{Al(OH)_3} + \underset{\text{Ethylammonium chloride}}{3EtNH_3Cl}.$$

$$CuSO_4 + \underset{\text{Methylamine}}{2CH_3NH_2} + 2H_2O = \underset{\text{pp.}}{Cu(OH)_2} + \underset{\text{Methylammonium sulphate}}{(CH_3NH_3)_2SO_4}.$$

$$NH_4Cl + \underset{\text{Aniline}}{PhNH_2} = \underset{\text{(Evolved)}}{NH_3} + \underset{\text{Phenylammonium chloride}}{PhNH_3Cl}.$$

In this last case the determining factor is the volatility of the NH_3 gas as compared with the aniline.

The "onium" bases.—Ammonium, phosphonium, arsonium, stibonium, $R_4M(OH)$, (R = hydrocarbon radicals, of which *one* may be an aryl group, M = N, P, As, Sb), sulphonium, $R_3S(OH)$, oxonium, $R_3O(OH)$ (itself unknown, salts known), carbonium—as triphenyl carbinol, $Ph_3C(OH)$ and iodonium, $Ph_2I(OH)$, form

salts in a perfectly similar manner to potassium or ammonium hydroxide, with elimination of water the hydroxides in the cases of $R_4M(OH)$ and $R_3S(OH)$ simulating the caustic alkalis closely.

$$\underset{\text{Tetrethylammonium hydroxide}}{Et_4NOH} + HCl = \underset{\text{Tetrethylammonium chloride}}{Et_4NCl} + H_2O.$$

$$\underset{\text{Triethylsulphonium hydroxide}}{2Et_3SOH} + H_2SO_4 = \underset{\text{Sulphate}}{(Et_3S)_2SO_4} + 2H_2O.$$

They can obviously pp. hydroxides of the metals.

$$\underset{\text{Ammonium hydroxide}}{3H_4NOH} + FeCl_3 = Fe(OH)_3 + 3H_4NCl.$$

$$\underset{\text{Tetrethylammonium hydroxide}}{3Et_4NOH} + FeCl_3 = Fe(OH)_3 + 3Et_4NCl.$$

Almost any cpd. containing the NH_2 or NH group can show basic properties, which, however, may not be apparent, owing to the presence of groups in the same molecule having acidic properties. Thus, nitraniline, $NO_2C_6H_4NH_2$, is neutral, NO_2 being an acidic group. It dissolves in strong HCl, however, and is ppd. by ammonia. Also aminoacetic acid, glycine, H_2NCH_2COOH, forms no true salts as an acid, but does form $ClNH_3CH_2COOH$. Even acid amides, $RCONH_2$, can form $RCONH_3Cl$, ppd. by HCl from an ethereal soln. of the amide.

CHAPTER XII.

ACID REACTIONS.

The typical group in organic acids is COOH, carboxyl, and true acids are mono-, di-, etc., basic as they possess one, two, etc., COOH groups.

Being acids, their positive ion is hydrogen, but the extent of ionisation is in general small, *i.e.* they are in general weak acids (VIII).

Bodies containing the group SO_3H are also acids, mono-, di-, etc., basic as containing one, two, etc., SO_3H groups, The ionisation in these cases is very complete, and they are comparable in strength with the strong mineral acids. Sulphinic acids are of type RSO_2H, and there are also phosphonic, phosphinic acids, *e.g.* $RPO(OH)_2$ and $R_2PO(OH)$ respectively.

As containing the OH group, all these show Reaction V. *c.*, replacement of hydrogen by sodium, and Reaction VI, replacement of OH by Cl (forming acid chlorides) by phosphorus halogenide, only that in this case, pentahalogenide never goes further than, *e.g.*, $POCl_3$, itself an acid chloride. The carboxyl halogenides, RCOCl, are decomposed by water, but *not* the sulphonyl halogenides, RSO_2Cl.

Other reactions are :—

a. **Reaction with inorganic base—Neutralisation.**

α. Base a hydroxide—phenolphthalein indicator.

$$\underset{\text{Carboxy acid}}{RCOOH} + \underset{\text{Hydroxide}}{HONa} = \underset{\text{Salt}}{RCOONa} + H_2O.$$

$$\underset{\text{Sulphonyl acid}}{RSO_2OH} + HONa = \underset{\text{Sulphonate}}{RSO_2ONa} + H_2O.$$

Here litmus or methyl orange may be used.

β. Base in form of carbonate. This "neutralisation" goes well enough if the acid be "strong," *i.e.* well ionised, like a sulphonic acid, not so well if a carboxylic acid, unless one of the stronger ones—the carbon dioxide requiring to be expelled by heating, otherwise the indication of end point is uncertain.

$$\underset{\text{Oxalic acid}}{\begin{matrix}COOH\\ |\\ COOH\end{matrix}} + K_2CO_3 = \underset{\text{Oxalate}}{\begin{matrix}COOK\\ |\\ COOK\end{matrix}} + CO_2 + H_2O.$$

$$\underset{\text{Trichloracetic acid}}{CCl_3COOH} + K_2CO_3 = \underset{\text{Trichloracetate}}{CCl_3COOK} + CO_2 + H_2O.$$

Both these give a definite end point with phenolphthalein, and the latter a fairly definite one with methyl orange, but this must not be used for carboxy acids in general.

b. **Removal of (weak) organic acids from their salts by mineral acids (strong).**

α. Organic acid sol., salt of mineral acid insol. and therefore ppd.

$$\underset{\text{Oxalate}}{\begin{matrix}COO\\ |\\ COO\end{matrix}\!\!>Ca} + H_2SO_4 = \underset{\text{(ppd.)}}{CaSO_4} + \underset{\text{(Soluble)}}{H_2C_2O_4}.$$

$$\underset{\text{Formate}}{(HCOO)_2Pb} + H_2S = \underset{\text{(pp.)}}{PbS} + \underset{\text{Volatile}}{2HCOOH}.$$

β. Organic acid insol., and therefore ppd., salt of mineral acid sol.

$$\underset{\text{Benzoate}}{PhCOOK} + HCl = \underset{\substack{\text{Benzoic acid}\\ \text{(ppd.)}}}{PhCOOH} + KCl.$$

c. Salts **of organic acids give precipitates with inorganic salts.**

α. Ferric chloride often forms insol. basic salts, as with benzoates.

$$2C_6H_5COOK + FeCl_3 + H_2O$$
$$= (C_6H_5COO)_2Fe(OH) + 2KCl + HCl.$$

β. Calcium chloride or sulphate gives insol. Ca salts.

$$\underset{\text{Oxalate}}{C_2O_4(NH_4)_2} + CaCl_2 = \underset{\text{(ppd.)}}{C_2O_4Ca} + 2NH_4Cl.$$

$$\underset{\text{Tartrate}}{C_4H_4O_6Na_2} + CaSO_4 = \underset{\text{(ppd.)}}{C_4H_4O_6Ca} + Na_2SO_4.$$

γ. Barium chloride acts similarly, in some cases.

$$\underset{\text{Succinate}}{\begin{matrix} CH_2COONa \\ | \\ CH_2COONa \end{matrix}} + BaCl_2 = \underset{\text{Ppd. especially in presence of alcohol}}{\begin{matrix} CH_2COO \\ | \\ CH_2COO \end{matrix}\!\!>\! Ba} + 2NaCl.$$

Owing to the solubility, *i.e.* decomposability, of most organic salts in mineral acids, these reactions do not happen in presence of free organic acid.

d. **Phenolic reactions.**

The aromatic tertiary OH bodies, mono-, di-, etc., behave as quasi-acids, reacting with alkaline hydroxides, forming water and a salt-like body, hydrolysed to some extent in any aq. soln. and completely so in much water. However, on heating the soln., water is expelled, and the salts are obtained in the solid condition. In some cases this salt formation occurs with oxides of the heavy metals.

Substitution by negative radicals, the halogens, NO_2, etc., in the ring, makes this acidic behaviour more pronounced, and the

more so as this substitution is increased, so that poly-haloid or -nitro phenols behave almost like true acids (see XVI). Substitution by groups, themselves acidic as SO_3H, $COOH$, has a similar effect on the OH, less marked, however, in the latter case, while substitution by positive radicals, as NH_2, diminishes the acidity of the OH even to zero. Thus aminophenol forms $HOC_6H_4NH_3Cl$ as a base more easily than $H_2NC_6H_4OK$—(quasi-) acidic.

$$\underset{\text{Phenol}}{C_6H_5OH} + NaOH = \underset{\text{Phenate}}{C_6H_5ONa} + H_2O.$$

$$\underset{\text{Naphthol}}{C_{10}H_7OH} + NaOH = \underset{\text{Naphtholate}}{C_{10}H_7ONa} + H_2O.$$

$$\underset{\text{Pyrogallol}}{C_6H_3(OH)_3} + 3NaOH = \underset{\text{Pyrogallate (?) easily decomposed}}{C_6H_3(ONa)_3} + 3H_2O.$$

$$\underset{\text{Trichlorphenol (1:2:4:6)}}{2Cl_3C_6H_2OH} + Na_2CO_3 = \underset{\text{Trichlorphenate}}{2Cl_3C_6H_2ONa} + CO_2 + H_2O.$$

$$\underset{\text{Picric acid (1:2:4:6)}}{2(NO_2)_3C_6H_2OH} + Na_2CO_3 = \underset{\text{Picrate}}{2(NO_2)_3C_6H_2ONa} + CO_2 + H_2O.$$

Here the power of decomposing carbonates has been acquired. The latter can be used as a test for potassium, the salt formed being so insol.

$$2Cl_3C_6H_2OH + PCl_5 = \underset{\text{Tetrachlorbenzene}}{2Cl_3C_6H_2Cl} + POCl_3 + HCl.$$

$$\underset{\text{Picric acid}}{(NO_2)_3C_6H_2OH} + PCl_5 = \underset{\text{Trinitrochlorobenzene}}{(NO_2)_3C_6H_2Cl} + POCl_3 + HCl.$$

Here "acid chlorides" are formed, and these are decomposed by water.

$$\underset{\text{Salicylic acid}}{C_6H_4{<}{\begin{matrix}OH & (1)\\ COOH & (2)\end{matrix}}} + 2NaOH = \underset{\text{Basic sodium salicylate}}{C_6H_4{<}{\begin{matrix}ONa & (1)\\ COONa & (2)\end{matrix}}} + 2H_2O.$$

This salt is largely hydrolysed by water like a phenate, one NaOH being removed.

$$2C_6H_4{<}{\begin{matrix}OH\\ COOH\end{matrix}} + 2Na_2CO_3$$

$$= \underset{\text{(Ordinary) Sodium salicylate}}{2C_6H_4{<}{\begin{matrix}OH\\ COONa\end{matrix}}} + CO_2 + H_2O.$$

e. The **"enolic" forms** of **β-ketonic acid** esters act similarly as quasi-acids.

CH_3COCH_2COOEt (Ethyl acetoacetate, ketonic form) passes into $CH_3C(OH){:}CHCOOEt$, enolic form, and this then reacts with NaOH but not with Na_2CO_3 forming $CH_3C(ONa){:}CHCOOEt$. These esters react also with ferric chloride, probably for a similar reason, *i.e.* the presence of a tertiary (OH) in them, cp. phenols, naphthols, etc.

f. *Primary and secondary nitrobodies* (but not tertiary, as nitrobenzene), *and monosubstituted haloid derivatives of the primaries*, but not of the secondaries, nor disubstituted primaries, also react with caustic alkalis as quasi-acids, eliminating water and forming salt-like bodies, probably as in the previous case by the passage into tautomeric forms containing an OH group.

Primary.	Secondary.	Primary monosubstit.
$CH_3CH_2NO_2$	$(CH_3)_2CHNO_2$	$CH_3CHBrNO_2$ respectively form
$CH_3HC{:}<\substack{ONa\\NO}$	$(CH_3)_2C<\substack{ONa\\NO}$	$CH_3CBr<\substack{ONa\\NO}$ or
$CH_3HC<\substack{O\\\dot{N}(ONa)}$	$(CH_3)_2C<\substack{O\\\dot{N}(ONa)}$	$CH_3BrC<\substack{O\\\dot{N}(ONa)}$

while $(CH_3)_3CNO_2$, tertiary, $CH_3CBr_2NO_2$, primary disubstituted, and $(CH_3)_2CBrNO_2$, secondary monosubstituted, do not form these cpds., having no replaceable hydrogen.

g. Certain other bodies can behave similarly.

Malonic and monosubstituted malonic esters react with alkylates forming *e.g.* sodio cpds.

$$(EtOOC)_2CH_2 + NaOEt = (EtOOC)_2CHNa + HOEt.$$
$$(EtOOC)_2CH_2 + 2NaOEt = (EtO_2C)_2CNa_2 + 2HOEt.$$
$$(EtOOC)_2CHEt + NaOEt = (EtO_2C)_2CNaEt + HOEt.$$

CHAPTER XIII.

CONDENSATIONS.

In these cases, as in VII, water is eliminated, but the products cannot well be classified under any of the groups previously considered there. They come nearer in some cases to acyl derivatives than to any other group.

Various cases are considered in the following :—

a. **Sulphonation,** forming sulphonic acids—by the action of conc. sulphuric or of fuming sulphuric (disulphuric) on bodies almost exclusively of the aromatic division and belonging to almost all groups in that division. Fatty sulphonic acids are known but are made otherwise (see I.).

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Sulphuric acid}}{HOSO_3H} = \underset{\text{Phenylsulphonic acid}}{C_6H_5SO_3H} + H_2O.$$

$$\text{or} \quad + 2HOSO_3H = \underset{\text{Benzene disulphonic acid}}{C_6H_4(SO_3H)_2} + 2H_2O \text{ etc.}$$

$$\underset{\text{Phenol}}{HOC_6H_5} + HOSO_3H = \underset{\text{Phenolsulphonic}}{HOC_6H_4SO_3H} + H_2O.$$

$$\underset{\text{Naphthalene}}{C_{10}H_8} + H_2SO_4 = \underset{\text{Naphthalenesulphonic } (\alpha \text{ or } \beta)}{C_{10}H_7SO_3H} + H_2O.$$

$$\underset{\text{Nitrobenzene}}{NO_2C_6H_5} + HOSO_3H = \underset{\text{Nitrobenzenesulphonic}}{NO_2C_6H_4SO_3H} + H_2O.$$

$$\underset{\text{Chlorbenzene}}{ClC_6H_5} + H_2SO_4 = \underset{\text{Chlorbenzenesulphonic}}{ClC_6H_4SO_3H} + H_2O.$$

$$\underset{\text{Aniline}}{NH_2C_6H_5} + H_2SO_4 = \underset{\text{Sulphanilic (1 : 4)}}{H_2NC_6H_4SO_3H} + H_2O.$$

$$\underset{\text{Benzoic}}{HOOCC_6H_5} + H_2SO_4 = \underset{\text{“Sulphobenzoic”}}{HOOCC_6H_4SO_3H} + H_2O.$$

$$\underset{\text{Anthraquinone}}{C_{14}H_8O_2} + H_2S_2O_7 = \underset{\text{Anthraquinonesulphonic acid}}{C_{14}H_7O_2SO_3H} + H_2SO_4.$$

b. **Nitration,** forming nitrobodies—by the action of conc. nitric acid, generally in presence of conc. sulphuric as condensing agent. This has the same range of application as sulphonation in general.

It does happen to some extent under special conditions with the higher fatty hydrocarbons, but fatty nitro-bodies are almost always made otherwise, three notable exceptions being mentioned among the examples.

$$\underset{\text{Toluene}}{CH_3C_6H_5} + \underset{\text{Nitric acid}}{HONO_2} = \underset{\text{Nitrotoluenes}}{CH_3C_6H_4NO_2} + H_2O\,(\text{to } H_2SO_4)$$

$$\text{or} \quad + 2HONO_2 = \underset{\text{Dinitrotoluenes}}{CH_3C_6H_3(NO_2)_2} + 2H_2O.$$

$$\underset{\text{Phenol}}{HOC_6H_5} + HONO_2 = \underset{\text{Nitrophenols}}{HOC_6H_4NO_2} + H_2O.$$

$$\underset{\text{Benzoic acid}}{HOOCC_6H_5} + HONO_2 = \underset{\text{Nitrobenzoic}}{HOOCC_6H_4NO_2} + H_2O.$$

$$\underset{\text{Phenolsulphonic}}{HOC_6H_4SO_3H} + 3HONO_2 = \underset{\substack{\text{Trinitrophenol}\\ \text{(picric acid)}}}{HOC_6H_2(NO_2)_3} + H_2SO_4 + 3H_2O.$$

Even oxidisable substs. like benzaldehyde with conc. HNO_3 give nitro derivatives.

Aniline, however, is oxidised largely, with production of much tarry matter, unless at very low temperatures, but acetanilide can be nitrated, giving o- and p-derivatives, whence o- and p-nitranilines can be obtained by hydrolysis.

$$\underset{\text{Acetanilide}}{AcNHC_6H_5} + HONO_2 = \underset{\text{Nitracetanilides}}{AcNHC_6H_4NO_2}(\text{o- and p-}) + H_2O.$$

$$\underset{\text{Nitracetanilides}}{AcNHC_6H_4NO_2} + NaOH = \underset{\substack{\text{Nitranilines}\\ \text{(o- and p-)}}}{H_2NC_6H_4NO_2} + NaOAc.$$

$$\underset{\text{Urea nitrate}}{NH_2CONH_3NO_3} + H_2SO_4 = \underset{\text{Nitrourea}}{NH_2CONH.NO_2} + (H_2O.H_2SO_4).$$

$$\underset{\text{Guanidine nitrate}}{NH_2C(NH)NH_3NO_3} + H_2SO_4$$

$$= \underset{\text{Nitroguanidine}}{NH_2C(NH).NHNO_2} + (H_2O.H_2SO_4).$$

The nitrates, formed by the usual method, are dissolved in conc. sulphuric at low temperatures.

$$\underset{\text{Urethane (Ethyl)}}{EtOOCNH_2} + \underset{\text{Ethyl nitrate}}{EtNO_3} + H_2SO_4 = \underset{\text{Nitrourethane}}{EtOOCNHNO_2} + EtOH + H_2SO_4.$$

Mix with well-cooled conc. sulphuric.

c. **Reaction with Nitrous Acid,** (i) for primary amino or amido cpds.

The reagent here is either—

α. The mixture of gases obtained by heating arsenious oxide with conc. nitric acid, or

β. Nitrite of sodium or potassium in presence of dil. acid (generally H_2SO_4), or

γ. Alkyl nitrite, *e.g.* amyl nitrite, and dil. acid.

There are various cases.

1. *Aliphatic primary amine* or *amide* and *aliphatic-aromatic primary amine* or *amide,* with (*β*) or (*γ*).

These give the corresponding hydroxy cpd., alcohol from amines, acid from amides, with elimination of nitrogen and water.

$$\underset{\text{Ethylamine and nitrous acid}}{\begin{array}{c|c|c} C_2H_5 & N & H_2 \\ + HO & N & O \end{array}} = \underset{\text{Ethyl alcohol}}{C_2H_5OH} + N_2 + H_2O.$$

$$\underset{\text{Acetamide and nitrous acid}}{\begin{array}{c|c|c} CH_3CO & N & H_2 \\ + HO & N & O \end{array}} = \underset{\text{Acetic acid}}{CH_3COOH} + N_2 + H_2O.$$

$$\underset{\text{Ethylene diamine}}{C_2H_4(NH_2)_2} + 2HONO = \underset{\text{(Ethylene) glycol}}{C_2H_4(OH)_2} + 2N_2 + 2H_2O.$$

$$\underset{\text{Succinamide}}{\begin{array}{l} CH_2CONH_2 \\ | \\ CH_2CONH_2 \end{array}} + \begin{array}{c} HONO \\ \\ HONO \end{array} = \underset{\text{Succinic acid}}{\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}} + 2N_2 + 2H_2O.$$

$$C_6H_5CH_2NH_2 + HONO = C_6H_5CH_2OH + N_2 + H_2O.$$
Benzylamine — Benzyl alcohol

$$C_6H_5CONH_2 + HONO = C_6H_5COOH + N_2 + H_2O.$$
Benzamide — Benzoic acid

2. The hydrochlorides of *aminoaliphatic acid esters* give diazo cpds., not, however, of the same type as the aromatic diazo cpds.

$$EtOOC.CH_2N(H)(H)(H)(Cl) + NaNO_2$$
Aminoacetic ethyl ester HCl

$$= EtOOCCH\begin{matrix}N\\ \|\\ N\end{matrix} + NaCl + 2H_2O.$$
Diazoacetic ester

3. **The Diazo Reaction.**

Salts of aromatic primary amines and (α) above or the amines themselves with (β) or (γ).

This is carried out in alcoholic soln. using the amines and (γ) when the free diazo salts are required.

$$2C_6H_5N(H)(H)(H)(Cl) + \text{“}N_2O_3\text{”} = 2C_6H_5NCl : N + 3H_2O.$$
Aniline HCl — (α) above — Benzene diazonium chloride

$$C_6H_5NH_2HCl + HCl + NaNO_2$$
Aniline-HCl

$$= C_6H_5NCl : N + NaCl + 2H_2O.$$
Phenyldiazonium chloride

$$CH_3C_6H_4NH_2 \longrightarrow CH_3C_6H_4NCl : N.$$
Toluidine — Tolyldiazonium chloride

$$(C_6H_5NH_3)_2SO_4 + 2NaNO_2 + 2H_2SO_4$$
“Aniline sulphate”

$$= 2N : N(C_6H_5)SO_4H + Na_2SO_4 + 4H_2O.$$
Phenyldiazonium sulphate

These simpler cpds. have the "diazonium" structure.

$HOC_6H_4NH_3Cl + HONO$
Aminophenol hydrochloride

$= HOC_6H_4NCl : N + 2H_2O$ (or $HOC_6H_4N : NCl$).
Diazophenol chloride

$SO_3HC_6H_4NH_2 + HONO$
Sulphanilic acid

$= HSO_3C_6H_4N(OH) : N + H_2O$ (or $HSO_3C_6H_4N : NOH$).
Diazobenzenesulphonic acid

$HOOCC_6H_4NH_2 + HONO$
Aminobenzoic acid
anthranilic if ortho.

$= HOOCC_6H_4N(OH) : N + H_2O$ (or $HOOCC_6H_4N:NOH$).
Diazobenzoic acid

In these latter cases of the diazohydroxy cpds. a further condensation seems to happen with formation of a ring anhydride.

$HOC_6H_4N:NOH$	$HSO_3C_6H_4N:NOH$	$HOOCC_6H_4N:NOH$
$C_6H_4 \begin{matrix} N:N \\ O \end{matrix} + H_2O$	$C_6H_4 \begin{matrix} N:N \\ SO_2.O \end{matrix} + H_2O$	$C_6H_4 \begin{matrix} N:N \\ \vert \\ CO.O \end{matrix}$
Diazophenol anhydride	Diazobenzene sulphonic anhydride	Diazobenzoic anhydride

d. **Nitrous acid** (ii).

Secondary amines, aliphatic and aromatic, give yellow oily liquids or crystalline bodies—nitrosamines.

$$Et_2NH + HONO = Et_2N.NO. + H_2O.$$
Diethylamine — Diethylnitrosamine

$$\begin{matrix} Ph \\ Me \end{matrix}>NH + HONO = \begin{matrix} Ph \\ Me \end{matrix}>N.NO. + H_2O.$$
Methylaniline — Methylphenylnitrosamine

$$Ph_2NH + HONO = Ph_2N.NO + H_2O.$$
Diphenylamine — Diphenylnitrosamine

Hydrazines as containing the NH group, *e.g.* $PhNHNH_2$, also give nitroso bodies.

$$PhNHNH_2 + HONO = PhN(NO)NH_2 + H_2O.$$

But in this case diazobenzene imide may be obtained.

$$PhN \begin{matrix} H & NH_2 \\ HO & N|O \end{matrix} \longrightarrow PhN < \begin{matrix} N \\ \vdots \\ N \end{matrix} \quad \left(\text{or } PhN{:}\underset{N}{\overset{\vdots}{N}}\,?\right)$$

Acyl anilides also containing the NH group, *e.g.* PhNHAc, also give nitroso bodies.

$$\underset{\text{Acetanilide}}{PhN(Ac)H} + HONO = \underset{\text{Nitrosoacetanilide}}{PhN(Ac)NO} + H_2O.$$

These bodies are identified by applying to them Liebermann's Reaction (*f*). They are hydrolysed by boiling with conc. acids, giving (salt of) secondary amine and nitrosyl cpd.

$$\underset{\text{Diethylnitrosamine}}{Et_2N.NO} + 2HCl = \underset{\text{Diethylamine-HCl}}{Et_2NH.HCl} + NOCl.$$

They are reduced to unsymmetrical hydrazines by Sn and HCl.

$$Et_2N.NO + 2H_2 = Et_2N.NH_2 + H_2O.$$

e. **Nitrous acid** (iii).

Tertiary dialkyl aromatic amines give paranitrosobodies as red HCl salts, passing into green bases with alkalis.

$$\underset{\text{Dimethylaniline-HCl}}{C_6H_5NMe_2HCl} + HONO = \underset{\text{p-nitrosodimethylaniline-HCl}}{NOC_6H_4NMe_2HCl} + H_2O.$$

$$\longrightarrow \underset{\text{p-nitroso, di-, etc. base}}{NOC_6H_4NMe_2.}$$

These paranitroso bodies are hydrolysed by boiling with alkalis, giving nitrosophenate and dialkylamine.

$$\underset{\text{p-NO-dimethylaniline}}{NOC_6H_4NMe_2} + KOH = \underset{\text{p-nitrosophenate}}{NOC_6H_4OK} + \underset{\text{dialkylamine}}{NMe_2H.}$$

f. **Nitrous Acid** (iv).

Aromatic hydroxy bodies (phenols, naphthols) give nitroso-bodies with nitrous acid and a condensing agent.

$$\underset{\text{Phenol}}{HOC_6H_5} + HONO = \underset{\text{Nitrosophenol}}{HOC_6H_4NO} + H_2O.$$

$$\underset{\text{Naphthols}}{HOC_{10}H_7\ (\alpha \text{ or } \beta)} + HONO = \underset{\text{Nitrosonaphthols}}{HOC_{10}H_6NO\ (\alpha \text{ or } \beta)} + H_2O.$$

These bodies are weak acids like the parent bodies. They appear to be identical (or desmotropic ?) with the monoximes of the corresponding quinones, regarded as diketones.

$$\underset{\text{Benzoquinone}}{O{:}C_6H_4{:}O} + H_2NOH = \underset{\text{Monoxime}}{O{:}C_6H_4NOH} + H_2O.$$

$$\underset{\text{Monoxime}}{O{:}C_6H_4NOH} \underset{\longleftarrow}{\longrightarrow} \underset{\text{Nitrosophenol}}{HOC_6H_4NO.}$$

They react with more of the HO body in presence of conc. H_2SO_4, giving intensely coloured substs. This is Liebermann's Reaction. Phenol itself gives first a brown, then a green, passing rapidly into deep blue. On diluting with water, the liquid becomes red, passing into blue again on adding alkali.

g. **Nitrous Acid** (v).

Primary and secondary nitro-bodies, or more probably their salts, react with nitrous acid in the following manner :—

1. Primary bodies give red salts of a "nitrolic" acid.

$$\underset{\text{Nitroethane}}{CH_3CH_2NO_2} \longrightarrow CH_3HC<^{NO}_{OK} + HONO = \underset{\text{Ethylnitrolate}}{CH_3C<^{(NO)_2}_{OK}}$$

$$\text{or} \longrightarrow CH_3HC<^{NOK}_{\dot{O}} + HONO = CH_3C(NO)<^{NOK}_{\dot{O}}.$$

2. Secondary bodies give blue pseudonitrol.

$$\underset{\text{Nitroisopropane}}{(CH_3)_2CHNO_2} + HONO \longrightarrow \underset{\text{Pseudonitrol}}{(CH_3)_2<^{NO}_{NO_2}} + H_2O.$$

3. Tertiary nitro bodies do not react. The aromatic nitro cpds., being of course tertiary, do not react, *e.g.* nitrobenzene

```
   HC  CH
HC<      >CNO2
   HC  CH
```

h. **The Isocyanide Reaction.**

This reaction appears to be common to *all substs.* containing the *primary amino* group, aliphatic and aromatic.

The amine is mixed with chloroform and alcoholic alkali in excess. The simpler (unsubstituted) isocyanides formed are characterised by a most offensive smell.

$$\mathrm{PhN}\begin{bmatrix}\mathrm{H} \\ \mathrm{H}\end{bmatrix} + \begin{bmatrix}\mathrm{Cl} \\ \mathrm{Cl} \\ \mathrm{Cl}\end{bmatrix} - \underset{\mathrm{H}}{\mathrm{C}} + 3KOH = PhNC + 3H_2O + 3KCl.$$

Aniline + Chloroform; PhNC = Phenylisocyanide

$$HOC_6H_4NH_2 + Cl_3CH + 3KOH$$
Aminophenol

$$= HOC_6H_4NC + 3KCl + 3H_2O.$$
Isocyanphenol

$$EtNH_2 + Cl_3CH + 3KOH = EtNC + 3KCl + 3H_2O.$$
Ethylamine

$$C_{10}H_7NH_2 + Cl_3CH + 3KOH = C_{10}H_7NC + 3H_2O + 3KCl.$$
Naphthylamine; Naphthyl isocyanide

j. **Direct formation of Amines from Aromatic Hydroxy Bodies.**

Aromatic hydroxy bodies in many cases can react with *ammonia*, forming amines directly, water being eliminated.

This does not happen to any appreciable extent with alcohols either of the aliphatic or of the aliphatic-aromatic division.

The substs. are heated under pressure in a sealed tube, the ammonia being generally used in the form of ammonio-zinc chloride, the $ZnCl_2$ removing the water.

$$C_6H_5OH + NH_3 = C_6H_5NH_2 + H_2O.$$
Phenol; Aniline

$$C_{10}H_7OH + NH_3 = C_{10}H_7NH_2 + H_2O.$$
Naphthols (α and β); Naphthylamines (α and β)

k. **The Friedel-Crafts Reaction,** with aluminium chloride (anhydrous) as condensing agent, assumes many forms. A number are discussed below.

a. *Aromatic hydrocarbons* and *halogen substituted hydrocarbons,*

fatty or aromatic, give *alkyl* or *aryl substituted hydrocarbons.* The mechanism of the reaction is shown in the next equation.

$$C_6H_5[H + Cl]Cl_5Al_2 \longrightarrow C_6H_5Al_2Cl_5 + HCl$$
Benzene — Double compound

$$C_6H_5Al_2Cl_5 + ClCH_3 \longrightarrow C_6H_5CH_3 + 2AlCl_3.$$
Double compound — Methyl chlor. — Toluene

$$2C_6H_5H + CH_2Cl_2 \longrightarrow (C_6H_5)_2CH_2 + 2HCl.$$
Methylene dichloride — Diphenylmethane

$$C_6H_5H + ClCH_2C_6H_5 \longrightarrow C_6H_5CH_2C_6H_5 + HCl.$$
Benzyl chloride — Diphenylmethane

$$C_6H_6 + 2CH_3Cl \longrightarrow C_6H_4(CH_3)_2 + 2HCl.$$
Xylenes

$$3C_6H_6 + CHCl_3 \longrightarrow HC(C_6H_5)_3 + 3HCl.$$
Chloroform — Triphenylmethane

A similar reaction may explain the use of aluminium amalgam in halogenation.

β. *Aromatic hydrocarbons* and *acyl chlorides* give *ketones.*

$$C_6H_5H + ClCOCH_3 \longrightarrow C_6H_5COCH_3 + HCl.$$
Benzene — Acetyl chloride — Acetophenone

$$C_6H_5H + ClCOC_6H_5 \longrightarrow C_6H_5COC_6H_5 + HCl.$$
Benzoyl chloride — Benzophenone

γ. *Carbonyl chloride* with *one molecule of benzene* gives *benzoyl chloride*, with *two molecules of benzene, benzophenone.*

$$C_6H_6 + ClCOCl \longrightarrow C_6H_5COCl + HCl.$$
Carbonyl chloride — Benzoyl chloride

$$2C_6H_6 + ClCOCl \longrightarrow C_6H_5COC_6H_5 + 2HCl.$$
Benzophenone

δ. *Aromatic hydrocarbons* and *carbon monoxide* (in presence of *cuprous chloride* as well) give aldehyde.

$$(1)\ CO + HCl = ClCHO$$
Chlorformaldehyde (?)

$$(2)\ C_6H_5[H + Cl]HCO = C_6H_5HCO + HCl.$$
Benzaldehyde

ε. *Aromatic hydrocarbons* and *cyanogen gas*, under slightly increased pressure, give aryl cyanides, *i.e.* acid nitriles.

$$C_6H_5H \quad + \quad (CN)_2 \longrightarrow \underset{\text{Phenyl cyanide}}{C_6H_5CN} \quad + \quad HCN.$$

ζ. *Aromatic hydrocarbons* and *carbamyl chloride* give *amides*.

$$C_6H_6 + \underset{\text{Carbamyl chloride}}{ClCONH_2} \longrightarrow \underset{\text{Benzamide}}{C_6H_5CONH_2} + HCl.$$

l. **The formation of esters of ketonic acids,** *e.g.* ethyl acetoacetate, is also a condensation, since it appears to take place by the condensation of two molecules of esters, the same or different, by the action of sodium ethoxide, alcohol being eliminated.

The stages are—

(i) $\underset{\text{(In the ester)}}{EtOH} + Na = \underset{\text{Ethoxide}}{EtONa} + \underset{\text{(evolved)}}{H.}$

(ii) $\underset{\text{Ethyl acetate}}{CH_3COOEt} + \underset{\text{Ethoxide}}{NaOEt} = CH_3C\begin{cases} OEt \\ OEt \\ ONa. \end{cases}$

Sodium diethyl orthoacetate

(iii) $CH_3C\begin{cases} \boxed{OEt} \\ \boxed{OEt} \\ ONa \end{cases} + \begin{matrix} H \\ H \end{matrix}\Big]\underset{\text{Ethyl acetate}}{CHCOOEt}$

$$= CH_3C(ONa){:}CHCOOEt + 2EtOH$$

(reacts with more Na).

(iv) On acidification—

$$CH_3C(ONa){:}CHCOOEt \longrightarrow CH_3COCH_2COOEt.$$

Generally—

$$RCOOEt \longrightarrow RC(OEt)_2(ONa) \longrightarrow RC(ONa){:}CH(CH_2)_nCOOEt.$$

With ester of form $CH_3(CH_2)_nCOOEt$.

CHAPTER XIV.

ALDEHYDE AND KETONE REACTIONS.

These reactions are not confined to aldehydes and ketones, but are so characteristic that it is convenient to bring them together here.

1. **Addition reactions.**

These probably always precede No. 2. They suggest that these bodies are unsaturated, but the unsaturation is due to the double linkage between carbon and oxygen in the carbonyl group found in both.

a. Addition of water forming *dihydroxy bodies*, stable only in soln. in much water. They have both OH groups on the same C atom forming "-ylidene glycols."

$$\underset{\text{Aldehyde}}{RHCO} + H_2O \longrightarrow \underset{\text{Alkylidene glycol}}{RHC(OH)_2}.$$

$$\underset{\text{Ketone}}{RRCO} + H_2O \longrightarrow \underset{\text{Dialkylidene glycol}}{RRC(OH)_2}.$$

The dihydroxy cpds. from substituted aldehydes are stable, *e.g.* chloral hydrate, $CCl_3HC(OH)_2$.

b. Fatty aldehydes (except HHCO) may add on *ammonia* forming *hydramines*, α-aminoalcohols. Simple ketones do *not* do so.

$$\underset{\text{Aldehyde}}{RHCO} + H.NH_2 \longrightarrow \underset{\text{Hydramine}}{RHC}{<}^{NH_2.}_{OH.}$$

c. Hydrocyanic acid is added on forming *cyanhydrins*, the nitriles of hydroxyacids, into which they pass on (acid) hydrolysis.

$$\underset{\text{Benzaldehyde}}{PhHCO} + HCN \longrightarrow \underset{\substack{\text{Benzald. cyanhydrin}\\ \text{Mandelonitrile}}}{C_6H_5.HCOH.CN} \longrightarrow \underset{\substack{\text{Phenylglycollic acid}\\ \text{Mandelic acid}}}{C_6H_5HCOHCOOH.}$$

$$\underset{\text{Acetophenone}}{PhCOCH_3} + HCN \longrightarrow \underset{\text{Nitrile of}}{{}^{Ph}_{CH_3}\!>C<^{OH}_{CN}} \longrightarrow \underset{\text{Phenylmethylglycollic acid}}{{}^{Ph}_{CH_3}\!>COH.COOH.}$$

d. Addition of *sodium bisulphite*, $H.SO_3Na$.

Both groups show this reaction, but methyl ketones do it so much more easily than other ketones that it was considered to happen only with them. The products are hydroxysulphonates, and are easily decomposed by acids and alkalis with liberation of the original cpd.

$$\underset{\text{Salicylaldehyde}}{HOC_6H_4HCO} + HSO_3Na = HOC_6H_4HC<^{OH}_{SO_3Na.}$$

$$\underset{\substack{\text{Methylphenylketone}\\ \text{acetophenone}}}{{}^{Ph}_{Me}\!>CO} + HSO_3Na = {}^{Ph}_{Me}\!>C<^{OH}_{SO_3Na.}$$

e. Two or more *aldehyde molecules* may unite.

α. Three molecules form ring cpds. See Polymerisation, XV.

β. Two molecules unite, forming various HO-aldehydes, by the action of mild condensing agents.

$$\underset{\text{2 Molecules acetaldehyde}}{H_3CHCO + HH_2CHCO} \longrightarrow \underset{\beta\text{-HO-butyraldehyde—aldol}}{H_3C.HCOH.H_2C.HCO.}$$

This is followed, on heating, by a condensation, see 2.

The addition product cannot be isolated in the case of ketones.

f. Addition of acyl anhydrides, forming esters having both acyl groups on the same C atom, "-ylidene" diesters.

$$\underset{\text{Aldehyde}}{RHCO} + \underset{\text{Acyl anhydride}}{Ac_2O} = \underset{\text{Alkylidene diacetate}}{RHC(OAc)_2}$$

Ketones do not show this reaction.

2. **Condensation Reactions,** with the usual elimination of water, etc.

Some of these are known to be preceded by addition of the reacting bodies, forming various OH bodies.

a. With *hydroxylamine* forming *oximes*, in presence of (mild) condensing agents (dry NaOAc).

$$H_3CHC[O + H_2]NOH = H_3CHCNOH + H_2O.$$
Aldehyde (acet-) — (Acet-)aldoxime

$$(CH_3)_2C[O + H_2]NOH = (CH_3)_2CNOH + H_2O.$$
Ketone (dimethyl) — Ketoxime (dimethyl)

With acyl anhydrides, these oximes react as follows:—

Aldoximes are dehydrated into nitriles, ketoximes form acyl esters.

$$H_3CHCNOH + Ac_2O = H_3CCN + 2HOAc.$$
Aldoxime (acet.) — Acetonitril

$$(H_3C)_2CNOH + Ac_2O = (H_3C)_2CNOAc + HOAc.$$
Acetoxime

These oximes behave as OH cpds, dissolving in alkalis.

b. With *phenylhydrazine*, under the same conditions, forming *phenylhydrazones.*

$$C_6H_5HC[O + H_2]NNHPh = C_6H_5HCN.NHPh + H_2O.$$
Benzaldehyde — Benzalphenylhydrazone

$$C_6H_5COCH_3 + H_2N.NHPh = C_6H_5C(NNHPh)CH_3 + H_2O.$$
Acetophenone

This reaction goes further with the complex hydroxyaldehydes and ketones—*the sugars, i.e.* reduction also happens, and dihydrazones called *osazones* result.

With *hydrazine* itself in two stages—*hydrazones* and *azines.*

$$H_3CHC[O + H_2]N.NH_2 = H_3CHCNNH_2 + H_2O.$$
Acetaldehyde — Hydrazine — Hydrazone

$$H_3CHCNN[H_2 + O]CHCH_3 = H_3CHCN.NCHCH_3 + H_2O.$$
Hydrazone — (Acet-)aldazine

$$(CH_3)_2CO + H_2N.NH_2 = (CH_3)_2CN.NH_2 + H_2O.$$
Acetone — Hydrazone

$$(CH_3)_2CN.NH_2 + OC(CH_3)_2 = (CH_3)_2CN.NC(CH_3)_2.$$
Ketazine

Similarly the complex hydroxy-aldehydes and ketones, the sugars, form similar but more complex products.

c. With *thioalcohols*, mercaptans, forming *thioethers*, having two alkylsulphyl groups attached to same C atom—*mercaptals* and *mercaptols*.

$$\underset{\text{Aldehyde}}{H_3CHC[O} + 2H]SEt = \underset{\text{Mercaptal}}{H_3CHC(SEt)_2} + H_2O.$$

$$\underset{\text{Ketone}}{(H_3C)_2C[O} + 2H]SEt = \underset{\text{Mercaptol}}{(H_3C)_2C(SEt)_2} + H_2O$$

The mercaptols can be oxidised, producing complex sulphones, one of which is sulphonal, the soporific.

d. They may condense with one another, *i.e. two aldehyde molecules, two ketone molecules*, or *one aldehyde* and *one ketone* molecule,—forming *unsaturated aldehydes or ketones.* This in the case of aldehydes follows the aldol addition.

$$\underset{\text{Aldehyde 2 molecules}}{CH_3HC[O + H_2]HCHCO} \longrightarrow \underset{\text{Unsaturated aldehyde Crotonaldehyde}}{CH_3HC{:}CH.HCO} + H_2O.$$

$$\underset{\text{Ketone 2 molecules}}{(CH_3)_2C[O + H_2]HCCOCH_3} \longrightarrow \underset{\text{Unsat. ketone—"Mesityl oxide"}}{(CH_3)_2C{:}CHCOCH_3} + H_2O.$$

$$\underset{\text{"Mesityl oxide"}}{(CH_3)_2C{:}CHCOCH[H_2} + O]C(CH_3)_2$$
$$= \underset{\text{Phorone}}{(CH_3)_2C{:}CHCOCH{:}C(CH_3)_2} + H_2O.$$

$$\underset{\text{Benzaldehyde}}{PhHC[O} + \underset{\text{Acetone}}{H_2]HCCOCH_3} = \underset{\text{Benzal acetone or cinnamyl methyl ketone}}{PhHC{:}HC.COCH_3} + H_2O.$$

Certain sugars of formulae $C_{12}H_{22}O_{11}$ (biose) and $C_{18}H_{32}O_{16}$ (triose), may be considered as formed by a similar condensation of two or more molecules of monose sugars, $C_6H_{12}O_6$, the condensation sometimes causing the disappearance of the characteristic aldehydic or ketonic group, the sugar formed then showing no longer the aldehyde or ketone reactions.

The reaction in *this* direction

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} = \underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O.$$

has not yet been realised, though sucrose has been synthesised from fructose and a derivative of glucose.

$$\underset{\text{Glucose}}{C_5H_{11}O_5HCO} + \underset{\text{Galactose}}{C_5H_{11}O_5HCO} \longrightarrow \underset{\text{Lactose}}{C_{11}H_{21}O_{10}HCO} + H_2O.$$

Similar reactions may be considered to result in forming complex carbohydrates such as starch (and cellulose?), the condensation being accompanied by polymerisation to a very large molecule in the case of starch. These again have not yet been realised.

For the reverse reaction see Hydrolysis.

e. Aldehydes, but not ketones, condense with *alcohols*, forming ethers having two alkyloxy groups attached to the same C atom —the *acetals*—hydrolysed by boiling with dil. HCl.

$$\underset{\text{Aldehyde}}{RHCO} + \underset{\text{Alcohol}}{2HOR'} = \underset{\text{"Acetal"}}{RHC(OR')_2} + H_2O.$$

f. Fatty aldehydes (except HHCO) and the aldehyde sugars react with conc. *alkali solns.*, forming various products, among them a brown resinous body of peculiar smell—"*aldehyde resin.*"

Aromatic aldehydes and HHCO (2 molecules) give a mixture of corresponding alcohol and salt of corresponding acid, by simultaneous oxidation and reduction.

$$\underset{\text{Benzaldehyde}}{\begin{matrix} C_6H_5HCO \\ C_6H_5HCO \end{matrix}} + KOH = \begin{matrix} C_6H_5CH_2OH & \text{Benzyl alcohol} \\ C_6H_5COOK. & \text{Potassium benzoate} \end{matrix}$$

Aromatic aldehydes (2 molecules) with alcoholic KCN condense to a hydroxy ketone, oxidised to a diketone with conc. nitric.

$$\underset{\text{Benzaldehyde}}{\begin{matrix} C_6H_5HCO \\ + \\ C_6H_5HCO \end{matrix}} = \underset{\text{Benzoïn}}{\begin{matrix} C_6H_5CHOH \\ | \\ C_6H_5CO \end{matrix}} \rightarrow \underset{\text{Benzil}}{\begin{matrix} C_6H_5CO \\ | \\ C_6H_5CO. \end{matrix}}$$

g. Aldehydes form complex *coloured condensation products* with *Schiff's Reagent, i.e.* rosaniline decolorised by SO_3H_2.

This is not a restoration of the original magenta colour.

h. Acetone with NH_3 forms bases called *diacetonamine* and *triacetonamine*, probably by intermediate formation of mesityl oxide and phorone, which then add on ammonia.

$$\underset{\text{Mesityl oxide}}{(CH_3)_2C{:}CHCOCH_3} + NH_3 = \underset{\text{Diacetonamine}}{(CH_3)_2C(NH_2)CH_2COCH_3}.$$

$$\underset{\text{Phorone}}{(CH_3)_2C{:}CHCOCH{:}C(CH_3)_2} + NH_3$$
$$= (CH_3)_2CCH_2COCH_2C(CH_3)_2.$$
$$\text{|——NH——|}$$
Triacetonamine

These are obviously not hydramines.

j. Acetone and some other ketones react with *sodium nitroprusside* in presence of ammonia forming *coloured products*.

k. Ketones condense with *nitrous acid* forming *isonitrosoketones*.

$$\underset{\text{Acetone}}{CH_3COCH[H_2} + O]NOH = \underset{\text{Isonitrosoacetone}}{CH_3COCHNOH}$$

Dialdehydes and diketones in most cases react similarly to the mono- bodies, but in two stages. Sometimes stereochemical considerations have to be invoked to explain the existence of isomeric bodies formed.

CHAPTER XV.

POLYMERISATION.

Polymerisation is the direct union of two or more molecules, without elimination of any part, to form a more complex molecule often of quite different structure and function. Aliphatic straight chain cpds. may form ring cpds., and ring cpds. more complex rings. It is a common reaction among unsaturated cpds. and in general is possible only among them, whether the unsaturated linkage is between carbon atoms or between carbon and other atoms, oxygen, sulphur, nitrogen, etc.

The change may occur spontaneously, *i.e.* through causes not immediately perceptible to us, these causes being internal to the molecules concerned.

It may be brought about by the action of a small quantity of mineral substance, conc. hydrochloric or sulphuric acids, caustic alkali soln., zinc chloride, etc.

A few typical cases are considered below.

a. Formation of Ring Compounds from various straight chain cpds., change reversible.

i. *Cyanic acid* and *chloride*, three molecules form one of *cyanuric acid* and *chloride.*

$$\left.\begin{matrix} HO \\ Cl \end{matrix}\right\} \begin{matrix} C \\ \vdots \\ N \end{matrix} + \underbrace{\begin{matrix} N \\ \vdots \\ C \end{matrix}}_{HO\,Cl} + \begin{matrix} C \\ \vdots \\ N \end{matrix} \left\{\begin{matrix} OH \\ Cl \end{matrix}\right. = \left.\begin{matrix} HO \\ Cl \end{matrix}\right\} \begin{matrix} C : N . C \\ \cdot \qquad \cdot\cdot \\ \underbrace{N : C . N}_{HO\,Cl} \end{matrix} \left\{\begin{matrix} OH \\ Cl \end{matrix}\right.$$

Triple linkage becomes double.

```
HN        CO        NH              HN — CO — NH
 ..   +    ..   +    ..    ——>       |         |
OC        NH        CO              OC — NH — CO
```

Double linkage becomes single.

ii. Formaldehyde, acetaldehyde, and other *aliphatic aldehydes*, but no aromatic aldehydes, pass into *ring cpds.*

```
        H2                            H2C
        C                                \
       //                 ——>          O   O
      O       O                        |   |
              ||                     H2C   CH2
   H2C        CH2                        \
      \\                                  O
        O
```

3 molecules formaldehyde ——> paraformaldehyde.

```
  CH3HC                                 CH3HC
      //
     O       O            ——>              O   O
             ||                            |   |
  CH3HC      CHCH3                   CH3HC   CHCH3
      \\                                  \ /
        O                                  O
```

Acetaldehyde 3 molecules ——> paracetaldehyde.

Double linkage becomes single.

The new bodies are heterocyclic rings and not aldehydes at all, not showing any aldehyde reactions.

In these cases the unsaturation is not entirely that of carbon, and the new cpds. can be depolymerised, passing back into the original cpd. on heating. This is generally the case in such cpds.

b. **Polymerisation irreversible, into ring cpds.**

Where the unsaturation is that of carbon atoms only, the new cpd. cannot as a rule be depolymerised.

i. *Acetylenic hydrocarbons* pass into *benzene hydrocarbons* on

heating under pressure, even the pressure produced by the heating.

$$\begin{array}{ccc} & CH & \\ HC & & CH \\ HC & & CH \\ & CH & \end{array} \longrightarrow \begin{array}{ccc} & CH & \\ HC & & CH \\ | & & \| \\ HC & & CH \\ & C & \end{array}$$

3 mols. acetylene give benzene.

$$3CH_3C\vdots CH \longrightarrow \begin{array}{ccc} & CH & \\ CH_3C & & CCH_3 \\ HC & & CH \\ & CCH_3 & \end{array}$$

3 mols. allylene give mesitylene.

Here triple linkage becomes alternately single and double (Kekulé) or passes into two single linkages and one centric one. (Baeyer-Armstrong).

ii. *Derivatives of acetylenic hydrocarbons* pass into *derivatives of benzene hydrocarbons.*

$$\underset{\text{Propiolic acid}}{3CH \vdots C.COOH} \longrightarrow \underset{\text{Trimesic acid (sym.)}}{C_6H_3(COOH)_3}.$$

$$\underset{\text{Monobromacetylene}}{3HC \vdots CBr} \longrightarrow \underset{\text{Tribrombenzene (sym.)}}{C_6H_3Br_3}.$$

c. **Polymerisation into chains : irreversible.**

i. *Aliphatic aldehydes* show a reaction, a peculiar kind of polymerisation, due to the unsaturated C:O group, and this, like Class 2 above, cannot be reversed. The O of the HCO becomes united with an H of the CH_3 of another molecule, thus forming a *hydroxy-aldehyde*—the *aldol condensation.*

$$\underset{\text{2 Molecules acetaldehyde}}{CH_3HCO + HCH_2HCO} \longrightarrow \underset{\text{Aldol}}{CH_3HCOHCH_2HCO}.$$

This may be followed by a true condensation whereby an unsaturated aldehyde is formed with elimination of water. See X. *a. a.*

ii. Somewhat similar to this is the change undergone by *aromatic aldehydes* when boiled with an alcoholic soln. of KCN, only it is the H of the HCO of one molecule which becomes attached to the HCO of the other, the resulting cpd. being a *secondary alcohol ketone.*

$$\underset{\text{1st mol.}}{PhHCO} + KCN = PhHC\begin{matrix} OK \\ CN \end{matrix}$$

$$PhC\begin{matrix} H \\ OK \\ |CN \end{matrix} + \underset{\text{2nd mol.}}{\begin{matrix} O \\ H] \end{matrix} C\,Ph} = \begin{matrix} Ph \\ H \end{matrix} > C \begin{matrix} OK \\ \end{matrix} - C \begin{matrix} O \\ Ph \end{matrix} \quad \text{and}$$

$$\begin{matrix} Ph \\ H \end{matrix} > C \begin{matrix} O|K + CN|H \\ \end{matrix} - C \begin{matrix} O \\ Ph \end{matrix} = \begin{matrix} Ph \\ H \end{matrix} > C \begin{matrix} OH \\ \end{matrix} - C \begin{matrix} O \\ Ph \end{matrix} + HCN$$

iii. *Ethylenic hydrocarbons* polymerise into *ethylenic hydrocarbons of longer chain,* the position of the double link changing.

Two molecules of isopropylethylene pass into diamylene, three into triamylene.

This may be represented thus, assuming conc. H_2SO_4 as the polymerising agent.

$$\left.\begin{matrix} Me_2CH.CH{:}CH_2 + H.SO_4H = Me_2CH.CH_2.CH[HSO_4H] \\ Me_2CH.CH{:}CH_2 + H.SO_4H = Me_2CH.CH_2.CH[HSO_4H] \end{matrix}\right\}$$

$$= Me_2CH.CH_2.CH{:}CH.CH_2CHMe_2 + 2H_2SO_4.$$

CHAPTER XVI.

INTRAMOLECULAR CHANGE.

This kind of reaction includes various cases where a subst. passes into another isomeric with it. In certain cases this appears to occur spontaneously, *i.e.* through causes unknown to us: in other cases we know the conditions and causes more or less completely. Perhaps the most interesting feature about the latter kind is that the change can in some instances be brought about by extremely small quantities of a third subst., and in this case the reaction is similar to some of those to be considered in the next section, viz. Fermentation, that is, the reaction in these cases, and possibly in all, is catalytic. It might be said that the catalytic agent adds itself on, in parts, to the cpd.—or is separated from the cpd.—then is separated in parts from the cpd. —or added on to it—in positions different from that which it had at first.

a. **Cyanate into Amide.**

Ammonium cyanate passes into *urea*.

Obviously NH_4OCN is an unsaturated body ; it may therefore add on *e.g.* H_2O, and this may again be separated from a different position in the molecule.

$$\underset{\text{Cyanate}}{NH_4OC\vdots N} + H_2O = \underset{\text{Am. carbamate}}{NH_4OCONH_2} - H_2O = \underset{\text{Urea}}{NH_2CONH_2}.$$

Here, of course, the reaction might also be supposed to take place by the elimination of water and addition of it:

$$NH_4OCN - H_2O = \underset{\text{Cyanamide}}{NH_2CN} + H_2O = NH_2CONH_2.$$

Both the suggested intermediate products are known, though not made in general by the first stage reaction. But cyanamide

is made by the desulphurisation of thiourea, by *e.g.* mercuric oxide.

$$\underset{\text{Thiourea}}{NH_2CSNH_2} + HgO = \underset{\text{Cyanamide}}{NH_2CN} + HgS + H_2O.$$

Similarly thiourea is obtained from ammonium thiocyanate by simple heating to 170° to 180°. This probably depends on a reaction quite similar to that for urea itself.

b. Amide into Imide.

Cyanamide behaves itself as if it existed in two forms, *Cyanogen amide,* $NC.NH_2$, and *carbon diimide,* $C(NH)_2$. Thus it gives the usual reactions characteristic of an amide; and like NH cpds., imines or imides, it contains replaceable hydrogen, forming, *e.g.* CN_2Ag_2, CN_2Ca.

Such behaviour is found in most amides. Thus *acetamide* reacts in some ways as if it had the formula $CH_3C(OH)NH$. Thus two ethers seem to be known, the O-ether, $CH_3C(OEt)NH$, the N-ether, $CH_3C(OH)NEt$. Similarly also benzamide, etc.

The forms are said to be "*tautomeric*" or "*desmotropic.*"

The passage of one form into another may be supposed to take place in a way quite similar to the above, and to the following.

c. Keto into Enol.

i. *Acetoacetic esters* also exist in two forms, one called

the *ketonic,* $CH_3CO.CH_2COOEt$, the other

the *enolic,* $CH_3C(OH){:}CHCOOEt$.

A given sample consists of an equilibrium mixture of these two, the quantities depending on temperature, etc.[1]

These may be supposed to pass into one another thus :—

CH_3COCH_2COOEt	like most ketones, can add on
H_2O	water, forming a glycol. This has two
$CH_3C(OH)_2CH_2COOEt.$	(OH) groups on one C, so eliminates
HO H	water, not from the same place, forming
$CH_3C(OH){:}CHCOOEt$	the enolic form.

[1] Recently both forms have been obtained separate at low temperatures.

These changes can then repeat themselves in the reverse direction—reforming the ketonic modification.

This substance and its homologues have therefore a double set of reactions corresponding to these tautomeric forms.

1. *Those belonging to the enolic form.*

a. It gives a colour reaction with ferric chloride. This is characteristic of tertiary hydroxy cpds.

b. The reaction with alkali metals and their alkylates, to form *e.g.* $CH_3C(ONa):CHCOOEt$.

c. Other metals form crystalline salts with these esters, *e.g.* copper forms $CH_3C(Ocu):CHCOOEt$.

2. *Those belonging to the ketonic form.*

a. The occurrence of the usual ketone reactions; condensations with hydroxylamine, phenylhydrazine, etc., forming oximes, phenylhydrazones, etc.

b. The replacement of the ketonic O by Cl_2, by the action of PCl_5. Thus—

$$CH_3COCH_2COOEt \text{ gives } CH_3CCl_2CH_2COOEt.$$

c. The hydrolysis giving ketones, thus

$$CH_3COCH_2COOEt \longrightarrow CH_3COCH_3 + HOCOOEt.$$

The reduction to β-hydroxy butyric (etc.) esters (or acid) might be evidence for either form, since the ketonic form naturally would give a secondary alcohol, and the enolic, being unsaturated, would add on H_2.

The homologues show similar forms and reactions.

ii. A similar tautomerism may be considered to exist among the *β-diketones*, which also react as *quasi-acids*. Thus acetyl acetone

$$CH_3COCH_2COCH_3 \longrightarrow CH_3C(OH):CHCOCH_3,$$

and this with copper acetate gives

$$CH_3C(Ocu):CHCOCH_3.$$

The corresponding beryllium cpd. is volatile and its vapour density corroborates the divalency of this metal.

d. Unsaturated Alcohols into Aldehydes and Ketones.

i. *Secondary unsaturated alcohols* pass into *saturated aldehydes* by a change similar to that described already for acetoacetic ester, or ammonium cyanate into urea.

$$RCH{:}CHOH \text{ adds on water} \longrightarrow RCH_2.CH(OH)_2.$$

Secondary unsaturated alcohol — Alkylidene glycol

$$RCH_2CH(OH)_2 \text{ separates water as usual} \longrightarrow RCH_2HCO.$$

Aldehyde

Thus vinyl alcohol can hardly be obtained in the free condition, passing into acetaldehyde so readily.

ii. Similarly *tertiary unsaturated alcohols* pass into *saturated ketones.*

$$RCH{:}C(OH)CH_3 \text{ passes spontaneously into } RCH_2COCH_3.$$

e. Symmetrical trihydroxy phenols, e.g. phloroglucinol, behave also as *triketones*, forming the usual oximes. These triketo-forms are derivatives of hexahydrobenzene or hexamethylene.

```
         C(OH)                                    C(OH)2
   HC  /     \  CH        adds on           H2C  /     \  CH2
      |       |           water 3 mols.         |       |
(HO)C  \     /  C(OH)                   (OH)2C  \     /  C(OH)2
          CH                                       CH2
```

Phloroglucinol as tri(OH) body.

```
                                         CO
This gives off        --->         H2C /    \ CH2
water as usual                        |      |
                                   OC  \    / CO
                                         CH2
```

Phloroglucinol as triketo-hexamethylene.

Similarly *paraquinones*, like benzoquinone, may be considered to behave as *peroxides*, having two oxygen atoms linked. But they also behave as *diketones*, forming mono- and dioximes. The change can be explained similarly.

$$\text{Quinone as peroxide} + 2H_2O = C_6H_4(C(OH)_2)_2 \longrightarrow C_6H_4(CO)_2 + 2H_2O$$

Quinone as peroxide — Quinone as diketone

f. Ortho-di-carboxy derivatives.

Certain presumably *symmetrical chain cpds.* react as if they had *unsymmetrical ring* structures. This succinyl chloride appears to be

$$\begin{matrix} CH_2CCl_2 \\ | \quad\quad >O \\ CH_2CO \end{matrix} \text{ not } \begin{matrix} CH_2COCl \\ | \\ CH_2COCl. \end{matrix}$$

Similarly, phthalyl chloride is

$$C_6H_4\begin{matrix} CCl_2 \\ \quad >O \\ CO \end{matrix} \quad \text{not} \quad C_6H_4\begin{matrix} COCl \\ COCl \end{matrix}$$

(ring atoms: HC, HC, HC, CH)

Phthalic aldehyde passes into phthalide similarly;

$$C_6H_4\begin{matrix} CHO \\ CHO \end{matrix} \longrightarrow C_6H_4\begin{matrix} CH_2 \\ \quad >O \\ CO \end{matrix}$$

g. Benzidine and Semidine transformations, etc.

i. The "Benzidine Transformation" is the name given to the change whereby a *symmetrical diarylhydrazine*, RNHNHR',

passes into a *diarylene diamine* by the action of acids, conc. hydrochloric generally. The simplest case is :—

$C_6H_5NH.NHC_6H_5$, hydrazobenzene
Symmetrical diphenylhydrazine

$\longrightarrow H_2NC_6H_4.C_6H_4NH_2$, benzidine.
Diphenylene para diamine

the NH_2 groups taking the para position to one another.

At the same time, some "diphenyline" or o-p-diphenylene diamine is formed.

NH . NH $\longrightarrow$ H_2N NH_2

When the para positions, or one of them is already filled, only one NH_2 group is found in the resulting body, this being called the **"Semidine Transformation"** and this may take the o- or p- position, the change being described as the o- or p- *Semidine Transformation.*

The change may be explained as follows :—

$C_6H_5NH.NHC_6H_5$, H Cl	hydrazobenzene, adds on HCl, splitting into
$C_6H_5NH_2$ and $ClNHC_6H_5$.	aniline and "phenylchloramine."
	The latter reacts with the aniline as
$NH_2C_6H_4[H + Cl]NHC_6H_5$	in Friedel-Crafts' Reaction, eliminating HCl.
$H_2NC_6H_4.NHC_6H_5$	This is the para-semidine reaction, if the aniline molecule makes a half rotation, the ortho-, if it does not.
$H_2NC_6H_4NHC_6H_5$ ClH	Semidine adds on HCl, splitting into chloraniline and aniline.
$H_2NC_6H_4Cl + H_2NC_6H_5$	
$H_2NC_6H_4[Cl + H]C_6H_4NH_2$	These react, eliminating HCl and thus
$H_2NC_6H_4 . C_6H_4NH_2$	giving the final product, benzidine, etc.

(ii) The following reactions are of the same type and can be similarly explained.

1. *Aromatic nitrosamines* pass into *para-nitroso-arylamines.*

$$C_6H_5N(CH_3)NO \longrightarrow ONC_6H_4NHMe.$$

Phenylmethylnitrosamine   p-Nitrosomethylaniline

$PhN(CH_3)NO$	phenylmethylnitrosamine
H Cl	adds on HCl splitting into
$PhNHCH_3 + NOCl$	methylaniline and NOCl.
	NOCl reacts with the para-H of
$CH_3NHC_6H_4[H + Cl]NO$	the aryl nucleus eliminating HCl
$CH_3NHC_6H_4NO + HCl$	forming p-nitrosomethylaniline.

2. *Aryl hydrazines* pass into *arylene p-diamines.*

$C_6H_5NHNH_2$	phenylhydrazine
H Cl	adds on HCl forming
$C_6H_5NH_2 + NH_2Cl$	aniline and NH_2Cl chloramine
	not isolable thus. It reacts with
$H_2NC_6H_4[H + Cl]NH_2$	a para-H of the aniline eliminating
$H_2NC_6H_4NH_2 + HCl$	HCl forming p-phenylene diamine.

3. *Formation of amino-azo-bodies.*

Diazo bodies react with arylamines, eliminating XH and forming diazoamino-bodies.

$$PhN{:}NCl + HHNC_6H_5 \longrightarrow PhN{:}N.NHC_6H_5 + HCl.$$

Phenyldiazochloride   Aniline   Diazoaminobenzene

The *diazoamino body* passes into a *para-amino-azo* body in presence of aniline-HCl, *i.e.* the HCl is added on again and the Cl in the diazo cpd. reacts with a para-H of the nucleus.

$$PhN{:}N[Cl + H]C_6H_4NH_2 \longrightarrow PhN{:}NC_6H_4NH_2.$$

Diazochloride   Aniline   Aminoazobenzene

h. **Secondary and Tertiary Aromatic Amines into Primaries.**

Alkyl-aromatic secondary amine-HCl salts heated to high temperatures (about 300°) in sealed tubes, pass into the isomeric *primary bases,* the alkyl passing to the nucleus.

$$\underset{\text{Methylaniline}}{C_6H_5NHMe.HCl} \longrightarrow \underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Methyl chlor.}}{MeCl} \longrightarrow \underset{\text{o- and p-Toluidine}}{MeC_6H_4NH_2.HCl.}$$

$$\underset{\text{Ethylphenylethylamine}}{EtC_6H_4NHEt.HCl} \rightarrow \underset{\text{Ethylphenylamine}}{EtC_6H_4NH_2} + EtCl \rightarrow \underset{\text{Diethylphenylamine}}{Et_2C_6H_3NH_2HCl.}$$

This change is obviously made up of two other reactions :—

a. The de-alkylation of the secondary base to primary base.
β. Friedel-Crafts Reaction applied to primary base (without the $AlCl_3$), causing alkylation in nucleus.

Similarly *dialkyl aromatic tertiary amine salts* give finally *dialkyl*-substituted *primary bases.*

$$\underset{\text{Dimethylaniline}}{C_6H_5NMe_2HCl} \rightarrow \underset{\text{Methylaniline}}{C_6H_5NMeH} + MeCl \rightarrow \underset{\text{Methyl toluidine}}{MeC_6H_4NHMe.HCl}, \text{ and}$$

$$\underset{\text{Methyl toluidine}}{MeC_6H_4NMeH.HCl} \rightarrow \underset{\text{Toluidine}}{MeC_6H_4NH_2} + MeCl \rightarrow \underset{\text{Xylidine}}{Me_2C_6H_4NH_2.HCl.}$$

Similarly, even *aromatic quaternary bases* change, thus phenyl-trimethylammonium iodide, $C_6H_5N(CH_3)_3I$, gives finally mesidine-HI $(CH_3)_3C_6H_2NH_2HI$.

j. The Beckmann Transposition.

The Beckmann Transposition is the change whereby *aldoximes* pass into *primary amides, ketoximes* into *secondary amides.* This is brought about by the action of such dehydrating agents as HCl gas, conc. sulphuric, phosphorus pentachloride, phosphoryl chloride, on the oxime in soln. in glacial acetic, etc., followed by rehydration by pouring the mixture into water or on to crushed ice.

$$\underset{\text{Aldoxime}}{RHCNOH} \longrightarrow \underset{\text{Primary amide}}{RCONH_2} \quad \Big| \quad \underset{\text{Ketoxime}}{RRCNOH} \longrightarrow \underset{\text{Secondary amide}}{RCONHR}$$

This is easily understood in the case of aliphatic aldoximes for these can be dehydrated (as by acetic anhydride) into nitriles, which, of course, can be hydrolysed into amides.

$$\underset{\text{Aldoxime}}{\begin{matrix} RC- \\ | \\ N- \end{matrix}\begin{bmatrix} H \\ \\ OH \end{bmatrix}} = \underset{\text{Nitrile}}{RCN} + H_2O = \underset{\text{Amide}}{RCONH_2.}$$

Thus acetaldoxime can give acetamide.

But aliphatic ketoximes with acetic anhydride give acetic esters.

$$RRCNOH + Ac_2O = RRCNOAc + HOAc.$$

Further, it is known that these oximes may exist in two stereoisomeric forms, according as the OH group is on the same side or not as a particular group in the cpd :—

R.CH = N(OH) R.C.R = N(OH) — Anti-oxime

R.C.H = N(HO) R.C.R. = N(HO). — Syn-oxime

In some cases both forms are known, in other cases only one exists. Anyhow, the configuration of a ketoxime can be determined by applying this Beckmann change.

RCR′ = N(HO) (Syn-oxime) ⟶ OCR′—RNH (Amide) | RCR′ = NOH (Anti-oxime) ⟶ RCO—HNR (Amide)

CH_3CPh = N(HO) (Synacetophenone oxime) ⟶ OCPh—CH_3NH (Methyl benzamide) | CH_3CPh = NOH (Antiacetophenone oxime) ⟶ CH_3CO—HNPh. (Acetanilide)

The mechanism of this change may possibly be represented as follows :—

$PhCC_6H_4CH_3$ = NOH (Synphenyl-tolyl ketoxime) $\xrightarrow{PCl_5}$ $PhCC_6H_4CH_3$ = NCl (Syn. "Nitrogen chloride") = Ph—Cl + $C.C_6H_4CH_3$ ≡ N (Elimination of PhCl leaving nitrile unsat.)

⟶ Cl—Ph + $CC_6H_4CH_3$ ≡ N (Addition of PhCl) ⟶ $Cl.CC_6H_4CH_3$ = PhN + H_2O ⟶

$ClCC_6H_4CH_3$—PhN with HO and H (eliminates HCl) ⟶ $OCC_6H_4CH_3$—PhNH (Toluic anilide)

$$\underset{\text{Anti-oxime}}{\overset{\displaystyle PhCC_6H_4CH_3}{\underset{NOH}{\|}}} \xrightarrow{PCl_5} \underset{\text{Anti-N-Cl}}{\overset{\displaystyle PhCC_6H_4CH_3}{\underset{NCl}{\|}}} \longrightarrow \underset{\text{Elimination of tolyl chloride}}{\overset{PhC}{\underset{N}{|||}} + \overset{C_6H_4CH_3}{\underset{Cl}{|}}}$$

$$\underset{\text{Addition}}{\overset{PhC}{\underset{N}{|||}} + \overset{Cl}{\underset{C_6H_4CH_3}{|}}} + H_2O \longrightarrow \underset{\text{Addition water}}{PhCCl(OH)NC_6H_4CH_3 \cdot H} \longrightarrow \underset{\text{Benzotoluide}}{\overset{PhCO}{\underset{HNC_6H_4CH_3}{|}}}$$

k. Phenyl-ester-acids into Phenol-acids.

Phenyl-ester acids, e.g. phenyl-carbonic and -sulphuric, are rather unstable and pass on heating into *phenol-carboxylic* and *-sulphonic acids*.

$$\underset{\text{Phenate}}{C_6H_5ONa} + CO_2 \longrightarrow \underset{\text{Phenylcarbonate}}{C_6H_5OCO_2Na} \longrightarrow \underset{\text{o-Hydroxybenzoate, i.e. salicylate}}{C_6H_4(OH)COONa}$$

$$\underset{\text{Phenol}}{C_6H_5OH} + HOSO_3H \longrightarrow \underset{\text{Phenylsulphuric}}{C_6H_5O \cdot SO_3H} + H_2O \longrightarrow$$

$$\underset{\text{o-phenolsulphonic}}{C_6H_4(OH)SO_3H}$$

In these cases some of the para cpd. is produced at a rather higher temperature, this change in the case of a salicylate being reversed at a still higher temperature. It is indeed a common enough change for aromatic ortho and para cpds. to pass into one another, especially on heating, though the change

into para cpd. is perhaps most frequent. Thus all the brom-sulphonic and di-sulphonic acids of benzene give resorcinol—which is meta—on potash fusion. So also isocyanides, aliphatic and aromatic, pass into cyanides (which may be regarded as a change for the better)—at temperatures above the b.p. of the isocyanides. However, some isocyanide is formed occasionally in reactions which normally ought to give cyanides, *e.g.* fusions with KCN (arylsulphonates) or in the reaction between halo-substituted cpds. and KCN, also in the Sandmeyer Reaction using cuprous cyanide.

l. **Aliphatic Nitro Derivatives.**

In most cases it is admitted that *aliphatic nitro cpds.* in the free condition have that structure, but there is strong evidence that the metallic derivatives are derived from the *enolic form*, e.g. $CH_3CH_2NO_2$ passes into

$$CH_3HC<{NO \atop OK} \text{ or } CH_3HC\left\langle {N(OK) \atop | \atop O} \right. \quad \text{derived from}$$

$$CH_3HC<{NO \atop OH} \text{ or } CH_3HC\left\langle {NOH \atop | \atop O} \right. .$$

This might (very hypothetically) be explained thus :—

$CH_3H_2CNO_2$	gives up
H_2O	water forming the
$CH_3C.N{:}O$	unknown cyanoxide.
H OH	This adds on the water again at another position producing the OH form.

$$CH_3HC<{NO \atop OH} \text{ or } CH_3HC\left\langle {NOH \atop | \atop O} \right.$$

In some cases both forms are known, as phenyl-nitromethane, $C_6H_5CH_2NO_2$, colourless oil, sol. in NaOH and regenerated from the soln. by acetic acid. But mineral acids pp. a crystalline form giving a red colour with $FeCl_3$ and acting in soln. as an electrolyte, therefore presumably $C_6H_5CH.NOH$ (with CH and N both bonded to O).

$$C_6H_5\underset{\diagdown\ \diagup \atop O}{CH.NOH}.$$

CHAPTER XVII.

FERMENTATION.

Enzymes.

This may be described as a process of chemical change due to the activity of living cells. These cells contain substs., called Enzymes, to which the actions are due, probably in all cases. In numerous cases these can be removed from the cells, without losing their activity.

Their action is catalytic, in general, sometimes reversible, like that of other catalysers. Some of the actions may be imitated by purely chemical methods, but, unlike most inorganic ferments, their action is specific, *e.g.* a fat-splitting enzyme cannot hydrolyse starch or glucosides. Probably in all cases they form definite combinations with the subst. fermented, with which they generally occur in the same natural source.

No enzyme has been obtained in the pure condition: they are ppd. from soln. by alcohol, or by salts such as $(NH_4)_2SO_4$ or Na_2SO_4 or carried down with neutral pps. formed in their presence, *e.g.* $Ca_3(PO_4)_2$. They invariably contain small proportions of inorganic matter, which in some cases seems to be of great importance, as in the case of a particular oxidising ferment containing Mn, Laccase, the activity of the ferment being proportional to the amount of Mn present.

They can act only within a limited temperature range, action ceasing at the freezing-point and a temperature of 60° causing fairly rapid destruction of the ferment, while at higher temperatures destruction is almost instantaneous. Generally enzymes of animal origin act best at about blood-heat, 37° C., those of vegetable origin at about 25° C. Also the action is favoured by neutrality of the soln. in general, or at least slightly acid solns. are preferable to slightly alkaline ones. Pepsin, the gastric enzyme, is most active in presence of ·2 per cent. HCl, trypsin (of pancreatic juice) in presence of 1-2 per cent. Na_2CO_3, Many neutral substs., very poisonous to the

living organism (cyanides, fluorides, $CHCl_3$, toluene), do not greatly inhibit enzyme action, so are added to solns. undergoing enzyme changes, to prevent bacterial contamination.

The chemical actions in fermentation, presumably—but not certainly—in all cases produced by enzyme action, can be classified as follows; using the numbers for the reactions as in the preceding sections.

1. **Oxidation Enzymes** "Oxidases."

a. Alcohol oxidase: in bacterium aceti. This causes the following changes:—

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH}.$$

$$\underset{\text{Mannitol}}{C_6H_{14}O_6} \longrightarrow \underset{\text{Fructose}}{C_6H_{12}O_6}.$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{Gluconic acid}}{C_6H_{12}O_7}.$$

$$\underset{\text{Glycol}}{CH_2OH.CH_2OH} \longrightarrow \underset{\text{Glycollic acid}}{CH_2OHCOOH}.$$

b. An *enzyme* in a similar organism called the *sorbose* bacterium acts thus:—

$$\underset{\text{Glycerol}}{C_3H_8O_3} \longrightarrow \underset{\text{Dihydroxyacetone}}{CH_2OH.CO.CH_2OH}.$$

$$\underset{\text{Sorbitol}}{C_6H_{14}O_6} \longrightarrow \underset{\text{Sorbose}}{C_6H_{12}O_6}.$$

$$\underset{\text{Mannitol}}{C_6H_{14}O_6} \longrightarrow \underset{\text{Fructose}}{C_6H_{12}O_6}.$$

The possibility of action here depends on the configuration of the alcohol. Also it oxidises aldehydes into acids and hydroxy-aldehydes further into ketonic acids.

$$\underset{\text{Glucose}}{CH_2OH.CHOH(CHOH)_3HCO} \longrightarrow$$

$$\underset{\text{Gluconic acid}}{CH_2OH.CHOH.(CHOH)_3COOH} \longrightarrow$$

$$\underset{\text{Ketogluconic acid}}{CH_2OH.CO.(CHOH)_3COOH}.$$

c. Uricolase: in the liver.

$$\underset{\text{Uric acid}}{C_5H_4N_4O_3} \longrightarrow OC\begin{cases} NH.CH.NH \\ \qquad\;\; | \\ NH_2\,CO.NH \end{cases}CO.$$

This is "allantoin," glyoxylic di-ureide.

d. "Peroxidases" activate H_2O_2 and other peroxides, inducing reactions impossible for these without them.

e. Catalase, and other oxidases, induce the decomposition of H_2O_2, but catalase may not be an oxidase itself, it may only remove the H_2O_2 often produced as a bye-product in other oxidations.

2. Reduction Enzymes "Reductases."

These probably occur in tissues having reducing properties. Yeast can convert free sulphur into H_2S, and some tissue extracts can reduce nitrates to nitrites and nitrobenzene to aniline.

7. Condensation.

Certain enzymes normally producing hydrolysis under special conditions can effect the reverse reaction.

By *Maltase.*

$$\underset{\substack{\text{Glucose,}\\\text{conc. soln.}}}{C_6H_{12}O_6} \longrightarrow \underset{\text{Maltose}}{C_{12}H_{22}O_{11}}.$$

By *Lipase.*

$$EtOH + \underset{\text{Butyric acid}}{C_3H_7COOH} \longrightarrow \underset{\text{Ethyl butyrate}}{C_3H_7COOEt}$$

9. Hydrolysis.

This is perhaps the most extensive enzyme action.

a. Of Polysaccharoses.

a. Diastase (amylase) in malt, etc.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} \longrightarrow \underset{\text{Dextrines}}{(C_6H_{10}O_5)_x} \quad \Big| \quad \underset{\text{Glycogen}}{(C_6H_{10}O_5)^m} \longrightarrow \underset{\text{Maltose}}{C_{12}H_{22}O_{11}}.$$

b. Inulase: in tubers, *e.g.* artichoke.

$$\underset{\text{Inulin}}{(C_6H_{10}O_5)_p} \longrightarrow \underset{\text{Fructose}}{C_6H_{12}O_6}.$$

No action on starch.

c. Cellulase: in germinating grain. Cellulose into reducing sugars.

β. Of disaccharoses.

a. Maltase (*Glucase*) in yeast and malt, etc.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6}.$$

It does not act on sucrose, but it can hydrolyse glucosides as emulsin can.

Maltose is not directly fermentible by yeast.

b. Lactase: in milk sugar yeast.

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} \longrightarrow \underset{\text{Galactose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}.$$

This enzyme causes reversion, the product from mixture being "iso-lactose" quite like lactose.

c. Invertase: (*Invertin*) in yeast, many parts of plants, etc.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

No action on maltose or lactose.

γ. Of glucosides.

a. Emulsin: in bitter almonds.

$$\underset{\text{Amygdalin}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\text{Glucose}}{2C_6H_{12}O_6} + \underset{\text{Benzaldehyde}}{C_6H_5HCO} + \underset{\text{Hydrocyanic acid.}}{HCN}.$$

$$\underset{\text{Mandelonitrile-glucoside}}{C_{14}H_{17}NO_6} + H_2O = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Benzaldehyde}}{C_6H_5HCO} + \underset{\text{Hydrocyanic acid}}{HCN}.$$

This cpd. is obtained from amygdalin by yeast.

$$\underset{\text{Salicin}}{C_{13}H_{18}O_7} \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Saligenin}}{(HO)C_6H_4CH_2OH}.$$

Helicin $C_{13}H_{16}O_7$ gives salicylaldehyde instead of saligenin.

$$\underset{\text{Arbutin}}{C_{12}H_{16}O_7} \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Quinol}}{(HO)C_6H_4(OH)}$$

$$\underset{\text{Populin}}{C_{20}H_{22}O_7} \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Saligenin}}{(HO)C_6H_4CH_2OH} + \underset{\text{Benzoic}}{C_6H_5COOH}.$$

b. Myrosin in mustard, etc., seeds.

$$\underset{\substack{\text{Sinigrin}\\\text{Pot. myronate}}}{C_{10}H_{18}NS_2O_{10}K} \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\substack{\text{Allyl}\\\text{isothiocyanate}}}{C_3H_5NCS} + KHSO_4.$$

c. Indimulsin in indigo plants.

Indican $\longrightarrow$ $C_6H_{12}O_6$(variety) + Indoxyl: passing by air oxidation into indigo-blue.

δ. Hydrolysis of urea into ammonium carbonate by "*urease*."

ε. Hydrolysis of fats and other esters by *lipase*. This occurs in pancreatic juice, in blood, in various oily seeds. Even such esters as salol (*q.v.*) are hydrolysed. When it acts on esters of "racemic" (dl) acids, the d- and l- esters are hydrolysed at different rates. It may cause reversion (ante).

θ. Hydrolysis of the complex nitrogenous bodies of physiological importance called proteins. This is important in digestion. Various amino acids, *e.g.* glycin (*q.v.*), are among the products.

[1]1. 2. 7. 9. **Alcoholic fermentation.**

This is the change whereby glucose passes into ethyl alcohol and carbon dioxide $C_6H_{12}O_6 \longrightarrow 2CO_2 + 2C_2H_5OH$. It includes examples of oxidation, reduction, condensation, hydrolysis,

[1] The numbers of these sections correspond to the preceding part of the summary of Reactions.

as far as some of the original groups in the glucose, or various of the hypothetical intermediate products are concerned. About 95 per cent. of the glucose undergoes the main reaction, the rest gives the bye-products, small quantities of succinic acid (only in presence of living cells), and of glycerol, and also the mixture of higher alcohols remaining behind when the EtOH is distilled off, and known as "fusel oil."

Various suggestions have been made as to the method of action.

$$\underset{\text{Glucose}}{CH_2OH.CHOH.CHOH.CHOH.CHOH.CHO} \longrightarrow$$

$$\underset{\text{2 molecules of Glyoeraldehyde}}{CH_2OH.CHOH.CHO + HCHOH.CHOH.CHO.}$$

$$\underset{\text{Glyceraldehyde}}{2CH_2OH.CHOH.CHO} - 2H_2O. \longrightarrow$$

$$\underset{\text{Pyruvilaldehyde}}{2CH_3.CO.CHO} + 2H_2O \longrightarrow \underset{\text{Lactic acid}}{2CH_3CHOH.COOH.}$$

$$\underset{\text{Lactic acid}}{2CH_3CHOH.COOH} \rightarrow 2CO_2 + \underset{\text{Ethyl alcohol}}{2CH_3CH_2OH.}$$

Lactic acid is, however, almost nonfermentible.

Besides these, there are also various fermentations producing acids, *e.g.* butyric acid ; and those concerned in coagulation or clotting as of blood.

APPENDIX I.

PREPARATION OF REAGENTS.

Bromine Water.—A saturated soln. containing some free Br.

Copper Acetate, Barfoed's Reagent.—A dil. soln. containing a few drops acetic acid.

Cuprous Chloride.—Dissolve Cu_2Cl_2 in c. HCl. Add copper turnings and let stand in a flask closed by rubber stopper until colourless. Pour off the soln. and mix with ammonia as required.

Alkaline Copper Tartrate, Fehling's Soln.—Dissolve 17·32 gm. $CuSO_4 5aq$. in water, making it up to 250 c.c. Similarly make a soln. containing 25 gm. NaOH and 87·5 gm. KNa tartrate. Mix equal vols. when required.

Hydrogen Peroxide.—Dilute the ordinary 3 per cent. soln. to ten times its volume.

Iodine in KI Aq.——A roughly N/10 soln. will do.

Iodic Acid.—Dissolve in water to N/10 soln. approximately, *i.e.* 1 gram to 60 c.c. soln.

Lead Acetate, Alkaline.—Mix $Pb(OAc)_2$ soln. with NaOH until the original pp. dissolves.

Potassium Mercuriodide, Mayer's Reagent.—Make up roughly to the compn. K_2HgI_4 from KI and $HgCl_2$.

β-Naphtholate of Sodium.—Dissolve 1 gm. β-naphthol in 50 c.c. caustic soda soln. This becomes coloured on keeping.

Sodium Nitroprusside soln. should be prepared when required by dissolving to a pale pink soln.

Phosphomolybdic Acid, Sonnenschein's Reagent.—Make a quantity of ammonium phosphomolybdate in the usual manner. Wash by decantation with dil. HNO_3. Dissolve in boiling *aqua regia.*

Alcoholic Potash.—(*a*) For hydrolysis 1 : 8 rectified spirit; (*b*) for elimination HX, 1 : 2.

Resorcinol in H_2SO_4.—Dissolve 1 gm. in 50 c.c. c. H_2SO_4. This becomes coloured on keeping.

Schiff's Reagent for Aldehydes.—Grind up fuchsine (magenta) with 50 parts of cold saturated sulphurous acid. Cork up and stand until colourless. Dil. with water to ·1000 vols.; or, dissolve in water and pass SO_2 into the soln. until colourless. An excess of SO_2 makes it less sensitive.

Schultz's Soln.—Add KI to syrupy $ZnCl_2$ soln. until saturated. Then add iodine until dark sherry colour.

Schweizer's Soln.—Dissolve a few grams $CuSO_4$ 5 aq. in 20 parts water with a few c.c. NH_4Cl.Aq. Pp. with a slight excess of NaOH Aq. Filter through cloth. Wash till sulphate is removed. Dissolve in minimum quantity NH_3 Aq. Filter through glass wool.

Alcoholic Silver Nitrate.—5 gms. dissolved in a little water made up to 50 c.c. with rectified spirits.

Ammoniacal Silver Nitrite, Tollens' Reagent.—Dissolve one part $AgNO_3$ in 10 vols. of conc. ammonia diluted with an equal vol. water. Add an equal vol. of ten per cent. NaOH Aq. This is more sensitive than that obtained by adding excess of ammonia to $AgNO_3$. Aq.

Zinc Copper Couple.—Zinc, in the forms of zinc dust, filings, or granulated, is mixed with a soln. of four parts of $CuSO_4$. 5aq. in 150 c.c. water. Shake well, until the Cu soln. is nearly decolorised. Pour off or filter off. Wash with water and with alcohol (fresh lots) two or three times. The rapidity of action will, of course, depend on the fineness of the product.

It may be obtained in the dry condition by shaking up zinc dust with one tenth its weight of CuO, both well dried, in a flask.

APPENDIX II.—TABULAR INDEX.

The compounds included are arranged: (1) according to their functional groups; (2) their order in homologous series. A number of them are introduced here for the sake of comparison, not as being important in themselves. Esters and similar derivatives have in some cases been entered beside their alcohol, etc., or acid; also certain isomers with the most important form. Subscript numbers to temperatures under B.P., *e.g.* 120_{12}, indicate the pressure in mm. in the determination; thus Lactic acid boils at 120° under 12 mm. pressure. Numbers in square brackets are M.P.'s, those in round brackets (120) are B.P.'s. "D" in a column of M.P. or B.P. means that the cpd. decomposes before changing state; "D" and a number, that it decomposes at that temperature while changing state. "C" after a number = circa. Dim. Pr. = diminished pressure, G = gas, L = liquid, S = solid not cryst., C = crystals, c = colourless, w = white, o = oily, t = thick, y = yellow, r = red, etc. In the column headed Scheme, the numbers refer to tests, group or confirmatory, in the Scheme, Chap. XX. "*d*" "*l*" = dextro, levo.

Group.	Name.	Formula.	Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
HYDROCARBONS. Paraffin.	Methane	CH_4	G.c.	−184	−160		XIX	15
	Ethane	$CH_3 . CH_3$	,,	−172	−93		,,	
	Propane	$CH_3CH_2CH_3$	,,		−45		,,	
	Butane	$CH_3CH_2CH_2CH_3$	,,		+1		,,	
	iso —	$(CH_3)_3CH$	,,		−17		,,	
	Pentane	$CH_3CH_2CH_2CH_2CH_3$ ...	L.c.	−147·5	37·5	$(CH_3)_4C.$(10°)	,,	
	iso —	$(CH_3)_2CHCH_2CH_3$ ...	,,		30		,,	
	Petroleum Ether	Mixture C_5H_{12}, C_6H_{14}, etc.	,,		50−60		,,	
	Ligroïn	Mixture C_7H_{16}, C_8H_{18}, etc.	,,		90−120		,,	
Olefine.	Ethylene	$CH_2 : CH_2$	G.c.	−169	−105		,,	16
	Propylene ...	$CH_3CH : CH_2$	,,		−40		,,	
	pseudo Butylene	$CH_3CH : CHCH_3$	,,		+1		,,	
	Amylene	$(CH_3)_2C : CHCH_3$	L.c.		+36		,,	
Acetylene.	Acetylene ...	$CH : CH$	G.c.	− 81	−83·6	tetrabrom.	,,	17
	Allylene	$CH_3C : CH$	,,	−110	23·5	[239° D.	,,	
	Dipropargyl ...	$HC : CH.CH_2.CH_2.CH : CH$	L.c.	− 6	85		,,	

TABULAR INDEX.

Group.	Name.	Formula.	Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
ALCOHOLS. Paraffin.	Methyl alc. ...	CH_3OH	L.c.	−95	66	w. $\frac{1}{4}CaCl_2$	X A,B, VIII A,B,	20
	Ethyl ,, ...	CH_3CH_2OH	,,	−130	78·4	w. $\frac{1}{4}CaCl_2$	,, ,, [& X AB	19
	Propyl ,, ...	$CH_3CH_2CH_2OH$	,,		97·4		,, ,, ,,	22
	iso — ,, ...	$CH_3CHOHCH_3$	,,	−86	82·7	Ac ester (90)	,, ,, ,,	23
	Butyl ,, ...	$CH_3CH_2CH_2CH_2OH$ ...	,,		117	Ac ,, (125)	,, ,, ,,	22
	iso — ,, ...	$(CH_3)_2CHCH_2OH$	,,	−108	108	Ac ,, (116)	,, ,, ,,	,,
	Amyl ,, ...	$CH_3.CH_2.CH_2.CH_2.CH_2.OH$	L.c.o.		137	Valerate (203·7)	,, ,, ,,	,,
	iso — ,, ...	$(CH_3)_2CH.CH_2.CH_2OH$	,,	−117	131·4	iso Valerate (194)		,,
	,, ,, ,, ...	$\begin{matrix}CH_3\\C_2H_5\end{matrix}>CHCH_2OH$ ...	,,		128·7			—
Olefine.	Vinyl ,, ...	$H_2C:CHOH \rightarrow CH_3HCO$ ...						—
	Allyl ,, ...	$H_2C:CHCH_2OH$	L.c.		96−7		XIX, X A,B, ,, ,,	23
Alkylates.	Methoxide, Na	CH_3ONa	S.c.		D		VII B ,, ,,	23
	Ethoxide, Na ...	CH_3CH_2ONa	,,		D		,, ,, ,,	,,
	Ethoxide, Al ...	$(C_2H_5O)_3Al$	,,		Dim. Pr.		,, ,, ,,	,,
ETHERS.	di-Methyl- ...	CH_3OCH_3	G.c.		−23		VII B, VIII B, or X A	24
	Methyl Ethyl-	$CH_3OC_2H_5$	,,		+11		,, ,, ,,	,,
	diEthyl- ...	$C_2H_5OC_2H_5$	L.c.	Below −80	34−5		,, ,, ,,	,,
	Ethylene Oxide	$\begin{matrix}H_2C\\H_2C\end{matrix}>O$	G.c.		12·5		,, ,, ,,	—
POLY-ALCOHOLS.	Glycol ...	$CH_2OH.CH_2OH$	L.c.t.	−17·4	197·5	Diacetyl Ester (186)	,, ,, ,,	25
	Glycerol ...	$CH_2OH.CHOH.CH_2OH$	,,	+17	290	Triacetyl ,, (258)	,, ,, ,,	,,
	Mannitol ...	$C_6H_8(OH)_6$	S.w.	166	D	Hexacetyl ,, [119]	,, ,, ,,	26
	Sorbitol (*d*) ...	,, $+H_2O$ ...	,,	110	D		,, ,, ,,	—

TABULAR INDEX.

Group.	Name.	Formula.	Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
MONOHALOID ESTERS. Chlorides.	Methyl Chlor. ...	CH_3Cl	G.c.	−104	−24		VII A., VIII, IX A	27
	Ethyl ,, ...	C_2H_5Cl	,,	−142	+12·5		,, ,, ,,	,,
	Propyl ,, ...	$CH_3CH_2CH_2Cl$ ...	L.c.		44		,, ,, ,,	,,
	iso — ,, ...	$CH_3CHClCH_3$ ...	,,		36·5		,, ,, ,,	30
	iso-Amyl ,, ...	$(CH_3)_2CHCH_2CH_2Cl$ ...	,,		100		,, ,, ,,	27
	Allyl ,, ...	$H_2C:CHCH_2Cl$ ...	,,		46		XIX ,, ,, ,,	30
Bromides.	Methyl Brom. ...	CH_3Br	,,		4·5		,, ,, ,,	27
	Ethyl ,, ...	C_2H_5Br	,,	−116	38·8		,, ,, ,,	,,
	Propyl ,, ...	$CH_3CH_2CH_2Br$ ...	,,		71		,, ,, ,,	,,
	iso — ,, ...	$CH_3CHBrCH_3$ ...	,,		59·5		,, ,, ,,	30
	iso-Amyl ,, ...	$(CH_3)_2CHCH_2CH_2Br$	,,		120		,, ,, ,,	27
	Vinyl ,, ...	$H_2C:CHBr$ ...	G.c.		16		,, ,, ,,	30
	Allyl ,, ...	$H_2C:CHCH_2Br$ ...	L.c.		71		XIX ,, ,, ,,	,,
Iodides.	Methyl Iod. ...	CH_3I	,,	−65	43	coloured in light.	,, ,, ,,	27
	Ethyl ,, ...	C_2H_5I	,,	−109	72		,, ,, ,,	,,
	Propyl ,, ...	C_3H_7I	,,	−99	102		,, ,, ,,	,,
	iso — ,, ...	$CH_3 . CHI . CH_3$ ...	,,	−91	89·5		,, ,, ,,	30
	iso-Amyl ,, ...	$(CH_3)_2CH . CH_2CH_2I$	,,		148		,, ,, ,,	27
	Allyl ,, ...	$H_2C:CHCH_2I$ ...	,,		101		XIX ,, ,, ,,	30

TABULAR INDEX

Group.	Name.	Formula.	Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
POLY-HALOID ESTERS. Chlorides.	Methylene Chlor.	CH_2Cl_2	L.c.		41		VII B, VIII, XIII	30
	Ethylene ,, ...	$CH_2Cl . CH_2Cl$ ...	,,	−36	84		VII A, ,, X	30
	Ethylidene ,, ...	CH_3HCCl_2	,,		58		,, ,, ,,	31
	Propylene ,, ...	$CH_3CHClCH_2Cl$ ...	,,		97		,, ,, ,,	30
Bromides.	Methylene Brom.	CH_2Br_2...	,,		98		VII B, ,, XIII	30
	Ethylene ,, ...	CH_2BrCH_2Br	,,	+9	131		VII A, ,, X	,,
	Ethylidene ,, ...	CH_3CHBr_2	,,		110		,, ,, ,,	31
	Propylene ,, ...	$CH_3CHBrCH_2Br$ ...	,,		141		,, ,, ,,	30
	Amylene ,, ...	$(CH_3)_2CBr . CHBrCH_3$	,,		170-80 D		,, ,, ,,	,,
Iodides.	Methylene Iod....	CH_2I_2	,,	+4	180 D	become coloured.	VII B, ,, XIII	30
	Ethylene ,, ...	$CH_2I . CH_2I$	,,	81	D	,,	VII A, ,, X	,,
	Ethylidene ,, ...	CH_3CHI_2	,,		178	,,	,, ,, ,,	31
	Propylene ,, ...	CH_3CHICH_2I... ...	,,		227 D	,,	,, ,, ,,	30
	Chloroform ...	$HCCl_3$	,,	−62	61·5		,, VIII C, XIV	31
	Bromoform ...	$HCBr_3$	,,	+7·8	151	often coloured.	,, ,, ,,	32
	Iodoform ...	HCI_3	C.y.	119		sublimes.	,, ,, ,,	,,
	Carbon tetrachlor.	CCl_4	L.c.	−19·5	76		VII A, XII	32

TABULAR INDEX.

Group.	Name.	Formula.	Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
Other Inorganic Esters.	Nitrite Methyl ...	CH_3ONO	G.c.		−12		VII A, VIII A, XII	33
	,, Ethyl ...	C_2H_5ONO	,,		+16		,, ,, ,,	,,
	,, iso-Amyl ...	$C_5H_{11}ONO$	L.y.		96		,, ,, ,,	,,
	Nitrate Methyl ...	CH_3ONO_2	L.c.		66		,, ,, ,,	,,
	,, Ethyl ...	$C_2H_5ONO_2$	,,	−112	86		,, ,, ,,	,,
	Sulphate Methyl ...	$(CH_3)_2SO_4$	,,		188		,, ,, ,,	,,
	,, Ethyl ...	$(C_2H_5)_2SO_4$	,,	−24·5	208 D		,, ,, ,,	,,
	...ric ...	CH_3SO_4H	L.c.t.		D		,, ,, ,,	34
		$C_2H_5SO_4H$	,,		D		,, ,, ,,	,,
		... SO_4H	,,		D		,, ,, ,,	,,
		..	G.c.		−21		VIII C, XIII	36
			S w.	162		Sublimes.	VII B, VIII C, XIII	38
				60−1			,, ,, ,,	—
						Sublimes 100°.	,, ,, ,,	43
							,, ,, ,,	38
							VI ,, ,,	36
							VII B ,, ,,	38
						[illegible]° − 5°.	,, ,, ,,	,,
							,, ,, ,,	43

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	Name	Formula		M.P.	B.P.		Scheme.	Page.
								38
							VI, VIII C., XIV	39
							,, ,, ,,	,,
							,, ,, XIII	36
							,, ,, ,,	,,
					52		XIX, VI, VIII C, ,,	,,
			,,		104		,, ,, ,, ,,	,,
		. ...	S.w.	15	50·5	? Polymer	—	
		...COCH₃	L.c.	−97	56·5		VIII A, XIII	40
	..	$(CH_3)_2C(OH)SO_3Na$ ...	C.w.	D			,, ,,	42
	...razone	$(CH_3)_2C . N . NHPh$ ...	C.y.	16	165_{91}		VII B ,, ,,	,,
	...ime	$(CH_3)_2CNOH$	C.c.	59	135		,, ,, ,,	,,
	...ethyl Ethyl ketone	$CH_3COCH_2CH_3$ ...	L.c.	−86	81		VIII A, XIII	40
	di-Ethyl —	$C_2H_5COC_2H_5$	,,		103		,, ,,	,,
CARBOHYDRATES.	Glucose (*d*)	$C_5H_6(OH)_5HCO$ ...	S.w.	146	D	$+H_2O(86)°$ Ac. ester	VI, VIII C	44
	— azone	$C_6H_{10}O_4(N . NHPh)_2$...	C.y.	217	,,	[111·2]	VI, VII B, VIII C	46
	Galactose (*d*) ...	$C_5H_6(OH)_5HCO$ ...	C.w.	168	,,	Ac. ester [142]	VI, VIII C	44
	— azone	$C_6H_{10}O_4(N . NHPh)_2$...	C.y.	206	,,		VI, VII B, VIII C	46
	Mannose	$C_5H_6(OH)_5HCO$ ..	C.w.	136	,,	} Osazone	VI, VIII	44
	Fructose	$C_4H_5(OH)_4COCH_2OH$	S.w.	95	,,	} = glucosazone	,, ,,	47
	Sorbose	$C_4H_5(OH)_4COCH_2OH$	,,	?	,,	Osazone [164]		,,
	Lactose	$C_{11}H_{13}O_2(OH)_4HCO$ ...	C.w.	205	,,	Osazone [200]	VI, VII B, VIII C	49
	Sucrose	$C_{12}H_{14}O_3(OH)_8$ ...	C.c.	160	,,			48
	Dextrin	$(C_6H_{10}O_5)_x$	S.y.	D			,, ,, ,,	52
	Starch	$(C_6H_{10}O_5)_n$	S.w.	D			,, ,, ,,	50
	Cellulose	$(C_6H_{10}O_5)_m$	,,	D			,, ,, ,,	52

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Group.	Name.	Formula.	Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
ACIDS. Saturated.	Formic acid ...	HCOOH	L.c.	8·6	100·6		VIII C, X A, XI	58
	Acetic ,, ...	CH_3COOH	,,	16·05	118		,, ,, ,,	57
	Propionic ,, ...	CH_3CH_2COOH	,,	−22	140	Et Ester (98·8)	,, ,, ,,	59
	Butyric ,, ...	$CH_3CH_2CH_2COOH$ ...	,,	−8	163	,, ,, (124)	,, ,, ,,	,,
	iso — ,, ...	$(CH_3)_2CHCOOH$ ...	,,	−79	155	,, ,, (110)	,, ,, ,,	,,
	Valeric ,, ...	$CH_3CH_2CH_2CH_2COOH$	L.c.t.	−59	186	,, ,, (144)	X ,,	,,
	iso — ,, ...	$(CH_3)_2CHCH_2COOH$ ...	,,	−51	163	,, ,, (135)	,,	,,
unsatd	Acrylic ,, ...	$H_2C : CHCOOH$ ...	C.c.	7	139−40	,, ,, (101−2)	XIX, X	,,
	Crotonic ,, ...	$CH_3CH : CH . COOH$ ...	,,	72	180−5	Me ,, (120·7)	,, ,,	,,
ACIDS, Mono. Halo substd.	Chloracetic acid ...	$ClCH_2COOH$	C.c.d.	62	185−7	Et Ester (144)	IX A, VII A, X	60
	di — ,, ...	$Cl_2CHCOOH$	L.c.	−4	190−1	,, ,, (158)	,, ,, ,,	,,
	tri — ,, ...	Cl_3CCOOH	C.c.d.	52	195	,, ,, (164)	IX A, VII A, VIII C	,,
	Bromacetic ,, ...	$BrCH_2COOH$	,,	50−1	208	,, ,, (159)	,, ,, X	,,
	α — propionic acid	$CH_3CHBrCOOH$ ...	C.c.	24·5	205	,, ,, (162)	,, ,, ,,	,,
	β — — ,,	CH_2BrCH_2COOH ...	,,	61·5		,, ,, $(69-70)_{10}$	,, ,, ,,	,,
Amino.	Carbamic acid ...	NH_2COOH	Acid	unknown		some salts		82
	Aminoacetic acid	NH_2CH_2COOH Glycin ...	C.c.	232−6	D	HCl salt C.c.	IV, XI	,,
Hydroxy.	Carbonic acid ...	HOCOOH	Acid	unknown exc.		soln. salts known		62
	Glycollic ,, ...	$HOCH_2COOH$	C.c.	80	D	Et Ester (160)	X	61
	Lactic ,, ...	$CH_3CHOHCOOH$ ...	L.c.t.	18	120_{12}	,, ,, (154·5)	III, VII B, XIII	,,
	Hydracrylic acid	CH_2OHCH_2COOH ...	In conc. soln		only			—
Keto, etc.,	Glyoxylic acid ...	$HC(OH)_2COOH$	C.c.		Volatile	in steam		—
	Pyruvic ,, ...	$CH_3COCOOH$	L.c.t.	13·6	61_{12}	(165−70 D) Et Ester (148−53)		68
	Acetoacetic acid ...	CH_3COCH_2COOH ...	,,		D		VII A B, XI	,,

TABULAR INDEX.

Group.	Name.	Formula.	Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
ACIDS, di-, etc.	Oxalic acid ...	COOH . COOH ...	C.w.	189		Sublimes 150°	III, XII	63
	,, ,, ...	$(COOH)_2 + 2H_2O$ ...	C.c.	101				
	Malonic ,, ...	$CH_2(COOH)_2$ ...	C.c.	132	D			62
	Methyl — acid...	$CH_3CH(COOH)_2$ ...	,,	130 D		Et_2 Ester (195)		,,
	Ethyl — ,, ...	$C_2H_5CH(COOH)_2$ ...	,,	111·5	160 D			,,
	Tartronic ,, ...	$(CHOH)(COOH)_2$ ...	,,	184 D		Et_2 Ester (222°)		—
	Mesoxalic ,, ...	$C(OH)_2(COOH)_2$ ...	C.c.d.	115	D	$C(OH)_2(COOEt)_2$[57)] [(200c)		—
	Succinic ,, ...	CH_2COOH ... CH_2COOH ...	C.c.	180 – 5	235 D		X A, XI, XII	62
	mono Brom — acid	$CHBrCOOH$ CH_2COOH } *d.l.* ...	,,	160	D			—
	di — — acid ...	$CHBrCOOH$ ... $CHBrCOOH$ ...	,,	200 D				—
	Malic (levo) ,, ...	$CHOHCOOH$ ... CH_2COOH ...	C.c.d.	100	D	Me_2 Ester (122_{12}, 242 D) Et_2 ,, (248 D)		—
	Tartaric dextro [acid	$CHOHCOOH$ ...	C.c.	167	,,		II B, VIII D, XII	66
	Racemic (*d*+*l*) ,,	$CHOHCOOH$ ...	C.c.e.	205	,,	(+ H_2O) Me_2 Ester [85] [(282)		—
	Citric acid ...	$C_3H_4OH(COOH)_3$ ...	C.c.	153	175 D	+ H_2O [100°D]	III, VIII D, XII	69
	Glutaric acid ...	$CH_2 < {CH_2COOH \atop CH_2COOH}$ ...	,,	97	303 D	Et_2 Ester (237)		—
	Adipic ,, ...	CH_2CH_2COOH ... CH_2CH_2COOH ...	,,	150 c	265_{100}	Et_2 Ester (245)		—

TABULAR INDEX.

Group.	Name.	Formula.	Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
ESTERS OF MONO-ACIDS.	Formate Methyl	$HCOOCH_3$	L.c.	−101	32·5		III, VII, etc. XI	72
	,, Ethyl	$HCOOC_2H_5$...	,,		54·4		,, ,, ,, ,,	,,
	,, Propyl	$HCOOC_3H_7$...	,,		81		,, VII, ,, etc., ,, XI ,,	,,
	Acetate Methyl	CH_3COOCH_3	,,	−99	57·5		,, ,, ,,	,,
	,, Ethyl	$CH_3COOC_2H_5$	,,	−84	77		,, ,, ,,	,,
	,, Propyl	$CH_3COOCH_2CH_2CH_3$ ...	,,	−92	101		,, ,, ,,	,,
	,, iso-Amyl	$CH_3COOCH_2CH_2CH(CH_3)_2$	,,		140			,,
	Carbamate M'th.	NH_2COOCH_3	C.c.	52	177		III, IV, VII, VIII	82
	,, Ethyl	$NH_2COOC_2H_5$	,,	50	180		,, ,, ,, ,,	,,
	Aminoacetate —	$NH_2CH_2COOC_2H_5$ ...	L.c.o.		149	HCl salt [144]	IV, IX	83
	Carbonate Meth.	CO_3Me_2	L.c.	+·5	91		III, VII, VIII	72
	,, Ethyl	CO_3Et_2	,,		126		,, ,, ,,	,,
	Chlorcarbon ,,	$ClCOOC_2H_5$... ...	,,		93	Me-Ester (72·5)	,, ,, ,,	,,
	Acetoacetic ,,	$CH_3COCH_2COOC_2H_5$ ...	,,		181		VII, VIII, XIII	75
ESTERS OF DI-ACIDS.	Oxalate Methyl	$(CH_3)_2C_2O_4$	C.w.	54	163		III, VII, VIII, X, XII	72
	,, Ethyl	$(C_2H_5)_2C_2O_4$	L.c.	−41	186		,, ,, ,, ,, ,,	,,
	Malonate Meth.	$CH_2(COOMe)_2$	,,	−80c	181			—
	,, Ethyl	$CH_2(COOC_2H_5)_2$	,,	−50	198			—
	Succinate Meth.	$C_2H_4(COOMe)_2$	C.c.	19	80_{10} 195		VII, VIII, XII	72
	,, Ethyl	$C_2H_4(COOEt)_2$	L.c.	−21	216		,, ,, ,,	,,
	Tartrate Meth.	$C_2H_4O_2(COOMe)_2$	C.w.	48	280		III, VII, VIII, XII	,,
	,, Ethyl	$C_2H_4O_2(COOEt)_2$	L.c.t.		280	B.P. 164_{20}	,, ,, ,, ,,	,,
	di-Aceto — ,,	$C_2H_2(OAc)_2(COOEt)_2$ ...	C.c.	63·5	290	di-Me-Ester [103]		—
	Citrate Methyl	$C_3H_5O(COOMe)_3$	,,	79	176_{16}		III, VII, VIII, XII	72
	,, Ethyl	$C_3H_5O(COOEt)_3$	L.c.t.		283		,, ,, ,, ,,	,,

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Group.	Name.	Formula.	Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
ACID DERIVATIVES. Anhydrides.	Acetic	$(CH_3CO)_2O$	L.c.		137		V, VI, X B, XI	77
	Propionic ...	$(CH_3CH_2CO)_2O$ ...	,,		168		,, ,, ,, ,,	,,
	Lactic	$O<\begin{matrix}CH(CH_3)CO\\COCH(CH_3)\end{matrix}>O$ ...	S.w.	128	255	"Lactide"	III, VII A, XIII	,,
	Succinic ...	$\begin{matrix}CH_2CO\\CH_2CO\end{matrix}>O$	C.c.	120	261		VI, X B, XI	,,
	Citraconic ...	$\begin{matrix}CH_3C.CO\\ \cdot\cdot \\ H\,C.CO\end{matrix}>O$	,,	7	213–4	Acid – [84 – 6]	VI, XIX	,,
ACID DERIVATIVES. Chlorides.	Acetyl	CH_3COCl	L.c.		55		V, VI, X B, XI, XII	76
	Propionyl ...	CH_3CH_2COCl	,,		80		,, ,, ,,	,,
	Chloracetyl ...	$ClCH_2COCl$	,,		106		,, ,, ,,	,,
	Carbamyl... ...	NH_2COCl	C.c.	50	61–2		V, IV, VII, X B	,,
	Carbonyl	$COCl_2$	G.c.		8		V, VI, XII	77
	Oxalyl	$\begin{matrix}COCl\\COCl\end{matrix}$	L.c.	–12	64		,, ,, ,,	,,
	Malonyl ...	$CH_2(COCl)_2$	,,		58_{27}			,,
	Succinyl ...	$\begin{matrix}CH_2CO\\CH_2CCl_2\end{matrix}>O$	,,	0	192		VI, VII, XI, XII	,,

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Group.	Name.	Formula.	Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
ACID AMIDES, etc.	Formamide ...	$HCONH_2$	L.c.		192–5 D		III, IV, VII A, XI, etc.	78
	Acetamide ...	CH_3CONH_2	C.c.	82–3	222		VII A, XI	,,
	Propionamide ...	$CH_3CH_2CONH_2$ ...	,,	72	213		VII A	,,
	Chloracetamide ...	$ClCH_2CONH_2$	,,	116	224–5		VII A, IX	,,
	Urea	$CO(NH_2)_2$	,,	132–3	D		III, IV, VII, etc.	80
	,, nitrate ...	Urea HNO_3	,,	163	,,		III, IV, VII, XII, etc.	,,
	,, oxalate ...	2 Urea $H_2C_2O_4$ ...	,,		,,		,, ,, ,, ,, ,,	,,
	Thiourea	$CS(NH_2)_2$	,,	180	,,			91
	Carbon di-Sulphide	CS_2	L.c.	–119	46·2			—
	Uric Acid ...	$C_5H_5N_4O_3$	S.w.	D	D		IV, VIII C, etc.	83
	Caffein	$C_5H(CH_3)_3N_4O_2 + H_2O$	C.w.	233	,,	Subl. 116°	,, ,,	—
	Oxamide	$CONH_2.CONH_2$ ...	S.w.	417 D			III, IV, VII, XII	81
	Oxamic Acid ...	$CONH_2COOH$	C.c.	210 D		Et-Ester C.w. [114–5]	III, IV, VII, VIII, XII	82
	Succinamide ...	CH_2CONH_2 / CH_2CONH_2	,,	200 D			IV, VII, XII	78
	Succinamic Acid	CH_2CONH_2 / CH_2COOH	,,	300 D			,, ,, ,,	82
	Asparagin ...	CH_2CONH_2 / $CHNH_2COOH$ ...	,,	234·5	D	$+ H_2O$	—	—
	Succinimide ...	CH_2CO / $CH_2CO > NH$ ...	,,	126	288	$+ H_2O$ [100°]	IV, VII, XII	—

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Group.	Name.	Formula.	Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
NITRILES and Derivatives.	Hydrocyanic Acid	HCN	G.c.	−10·2	26·5		III, IV, VII B, XI	85
	Acetonitril ...	CH_3CN	L.c.	−44	81·6		IV, VII B, XI	87
	Propionitril ...	C_2H_3CN	,,	−103·5	98		IV, VII B, XI	,,
	Cyanic Acid ...	HOCN	?		0°D		III, IV, VII B	88
	— Chloride ...	ClCN	G.c.	−15c.	15		,, ,, ,,	—
	iso-Cyanate Methyl	CH_3NCO	L.c.		44		III, IV, VII, XIV	89
	,, Ethyl ...	C_2H_5NCO	,,	—	60		,, ,, ,, ,,	,,
	Cyanuric Acid ...	$C_3H_3N_3O_3 + 2H_2O$	C.w.	—	—		III, IV, VII	—
	,, Chloride	$C_3N_3Cl_3$	,,	146	190		,, ,, ,,	—
	,, Ethyl ...	$C_3N_3O_3Et_3$	,,	29	275	iso-Ester[95](276)	III, IV, VII, XIV	—
	Thiocyanic Acid ...	HSCN	?		0°D		III, XI	90
	,, Ethyl	EtSCN	L.c.		142	iso-Ester (133)	III, VII, XI	,,
	iso ,, Allyl	C_3H_5NCS	L.y.		150·7		,, ,, ,, ,,	,,
	Cyanogen	C_2N_2	G.c.	−34	−21		III, IV, VII, XI	85
	Malononitril ...	$CH_2(CN)_2$	C.c.	30	218			—
	Cyanacetic acid ...	$CH_2CNCOOH$ ...	C.y	66		Et-Ester (205-8)		—
	Succinonitril ...	$(CH_2CN)_2$	S.c.	54·5	158_{20}		IV, VII, XI	—
	Acetylcyanide ...	CH_3COCN	L.c.		93		—	—

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AROMATIC GROUP.

Group.	Name.		Formula.	Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
HYDROCARBONS.	Benzene ...	...	C_6H_6	L.c.	5·4	80·4	Thiophen (84)	XVIII, XIX	92
	Toluene ...	...	$C_6H_5CH_3$	,,	−92	110·3		VIII B, XVIII, XIX, XI	,,
	Xylenes ...	o	$C_6H_4(CH_3)_2$	,,	−28	142		,, ,, ,, ,,	,,
		m			−54	139			,,
		p			+15	138			,,
	Naphthalene	...	$C_{10}H_8$	C.w.	80	218		,, ,, ,, ,,	95
	Anthracene	...	$C_{14}H_{10}$	C.c.	216	360	Coml.-yellow	VIII A	96
	Phenanthrene	...	$C_{14}H_{10}$	,,	100	340	,, ,,	,,	,,
	Diphenylmethane		$(C_6H_5)_2CH_2$	,,	26·5	261		VIII B, XIII	94
	Triphenylmethane		$(C_6H_5)_3CH$	,,	93	358		VIII B	,,
	Ethylbenzene	...	$C_6H_5CH_2CH_3$ ...	L.c.		134		VIII B, XI, XIX	,,
	Diphenyl ...	...	$C_6H_5C_6H_5$	C.c.	70·5	255			,,
	Dibenzyl ...	...	$C_6H_5CH_2.CH_2Ph$ ...	,,	52	284			,,
	Styrolene...	...	$C_6H_5C:CH_2$ ...	L.c.		144		VIII B, XIX	,,
	Ph-Acetylene	...	$C_6H_5C:CH$ ...	,,		139		VIII B and D, XIX	95
	Stilbene ...	...	$C_6H_5CH:CHC_6H_5$	C.c.	124	306		,, ,,	,,

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Group.	Name.	Formula.		Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
HALOGEN DERIVATIVES.	Chlorbenzene ...	C_6H_5Cl	...	L c.	−40	132		IX A	97
	Brom — ...	C_6H_5Br	...	,,	−31	155		,,	,,
	Iodo — ...	C_6H_5I	...	,,	−30	190	Red in light	,,	,,
	di-Chlor — ...	$C_6H_4Cl_2$ ...	o	,,		179		,,	,,
			m	,,	−18	172			
			p	C.c.	+53	172			
	di-Brom — ...	$C_6H_4Br_2$ ...	o	L.c.	−1	224		,,	,,
			m	,,	+1?	219			
			p	C.c.	89	219			
	Chlor Toluene ...	$CH_3C_6H_4Cl$ ...	o	L.c.	−34	156		VIII B, IX A	,,
			m	,,	−48	150			
			p	,,	+7	163			
	Brom — ...	$CH_3C_6H_4Br$ ...	o	,,	−26	181		,, ,,	,,
			m	,,	−40	183			
			p	C.c.	+28	184			
	Iodo — ...	$CH_3C_6H_4I$ ...	o	L.c.		204	become red in light		
			m	,,		204		,, ,,	,,
			p	C.c.	35	211			
	Brom-Naphthalene	$C_{10}H_7Br$ ...	α	L.c.	5	279		,, ,,	,,
	,, ,, ...	,, ...	β	C.c.	59	282		,, ,,	,,

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Group.	Name.	Formula.		Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
NITRO DERIVATIVES. Aromatic.	Nitro-Benzene	$C_6H_5NO_2$		L.y.	5·6	209		IX A, XIV	99
	di- — — ...	$C_6H_5(NO_2)_2$		C.c.	116	319	c. if pure often	,, ,,	100
				,,	90	303	[yellow (297)		
				,,	172	299			
	Nitro-Toluene	$CH_3C_6H_4NO_2$		L.y.	+10·5	218		VIII B, IX A, XIV	99
				,,	16	230			
				C.y.	54	237			
	di- — — ...	$CH_3C_6H_3(NO_2)_2$	1.2.4	,,	70			,, ,, ,,	100
			1.2.5	,,	48				
			1.3.4	,,	6·1				
			1.3.5	,,	9·2		Volatile in steam		
	Nitro-Xylenes	$(CH_3)_2C_6H_3NO_2$	1.2.4	,,	29			,, ,, ,,	99
			1.4.5	L.y.o.		239			,,
	— Naphthalene	$C_{10}H_7NH_2$ ...	a	C.y.	61	304			,,
Aliphatic.	Nitro-Methane	CH_3NO_2		L.c.	−28·5	101	Salts $CH_2<^{NOM}_{\dot{O}}$	—	100
	— Ethane ...	$C_2H_5NO_2$		,,		113·4	,, $CH_3HC<^{NOM}_{\dot{O}}$	—	,,

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Group.	Name.	Formula.	Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
AMINES, AROMATIC. Primary and Derivatives.	Aniline	$C_6H_5NH_2$ ...	L.c.o.	−6·5	182	often yellow or red	VIII A, X B, XIV, XV	102
	,, hydrochloride	$C_6H_5NH_2HCl$ ...	C.c.	192		Sublimes	,, ,, ,, ,,	,,
	,, sulphate ...	$2C_6H_5NH_2H_2SO_4$	,,		D		,, ,, ,, ,,	,,
	Toluidines ...	$CH_3C_6H_4NH_2$ ...	L.c.o.	−21	199·7	coml.—red oils	,, ,, ,, ,,	,,
			,,		199	,, ,,		
			C.c.	45	198			
	Xylidines... ...	$(CH_3)_2C_6H_3NH_2$	L.c.o.		212−26	coml.—red oils		,,
	tri-Bromaniline ...	$C_6H_2Br_3NH_2$ ...	C.c.	119			VIII A, X B, XIV, XV	106
	Nitranilines ...	$NO_2C_6H_4NH_2$ o	C.y.	71	Steam	Ac. deriv. [92]	IX, X B, XIV, XV	,,
		m	,,	114	285	,, [142]		
		p	,,	147		,, [207]		
	Phenylene diamine	$C_6H_4(NH_2)_2$ o	C	102	252	Bases and salts	VIII A, X B, XIV, XV	107
		m	color-	63	287	generally colored		
		p	ed	147	267			
	Benzidine ...	$(C_6H_4NH_2)_2$ ...	C.c.	127·5	400	H_2SO_4 salt rather insol.	X B, XIV, XV	,,
	Naphthyl amines	$C_{10}H_7(NH_2)$ α	color-	50	300		VIII A, X B, XIV, XV	105
		β	ed	112	294			
AMINES. Secdy.	Phenyl Isocyanide	C_6H_5NC	L.c.		166 D	soon colored		
	Tolyl ,, o	$CH_3C_6H_4NC$ ...	,,		75_{16}	,, ,,		
	p		,,		99_{32}	,, ,,		
	Methylaniline ...	$C_6H_5NHCH_3$ ...	L.c.	−80	192	coml. colored { Ac. deriv. [101](253)	X B, XV	108
	Ethyl — ...	$C_6H_5NHC_2H_5$ ...	,,	−80	204	,, [54](258)	,, ,,	,,
	Diphenylamine ...	$C_6H_5NHC_6H_5$ ...	C.c.	53	310		,, ,,	109
AMINES. Terty.	Dimethylaniline...	$C_6H_5N(CH_3)_2$ ...	L.c.	2·5	192	coml.—colored		110
	Diethylaniline ...	$C_6H_5N(C_2H_5)_2$	,,	−39	213·		,, ,,	,,
	Triphenylamine...	$(C_6H_5)_3N$ ...	C.c.	+127		Sublimes : no salts	,, ,,	111

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Group.	Name.	Formula.		Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
SULPHONIC DERIVATIVES. Acids.	Phenyl sulphonic	$C_6H_5SO_3H \cdot 2H_2O$ ...		C.c.	50	D	Sulphone [128](276) K salt $\frac{1}{2}H_2O$	XVI, XI	120
	Tolyl — —	$CH_3C_6H_4SO_3H$		,,	92	,,		VIII B ?, XVI, XI	,,
	α-Naphthyl —	$C_{10}H_7SO_3H + H_2O$ ...		C.c.d.	90	,,	Cl [66]	XVI, XI	,,
	β- — ...	$C_{10}H_7SO_3H + H_2O$ ...		,,	161	,,	Cl [76]	,, ,,	,,
Chlorides.	Phenyl — chlor.	$C_6H_5SO_2Cl$		L.c.	14·5	251 D	Et(156_{15})	VI, XVI, XI	122
	Tolyl — —	$CH_3C_6H_4SO_2Cl$ ...	o	,,				,, ,, ,,	,,
			m	,,					
			p	C.c.	69	145_{15}			
Amides.	Phenyl — amide	$C_6H_5SO_2NH_2$ ...	...	,,	150	D		VII, XVI, XI	123
	Tolyl — —	$CH_3C_6H_4SO_2NH_2$	o	,,	155	,,		,, ,, ,,	,,
			m	,,	107			,, ,, ,,	,,
			p	,,	137			,, ,, ,,	,,
Di-Acid.	Benzene di-Sulph. acids	$C_6H_4(SO_3H)_2$ ...	o	,,		,,	Cl [105] NH₂ [233]	XVI, XI	,,
			m	,,			Cl [63] NH₂ [228]		,,
			p	,,			Cl [132] NH₂ [288]		,,
	Aniline sulph'nic	$NH_2C_6H_4SO_3H$ ...	o	C.c.e.	280D	,,	+ $\frac{1}{2}$ aq.		
			m				"Metanilic" + $1\frac{1}{2}$ aq.		,,
			p				"Sulphanilic" + 2aq.	VIII A, etc.	,,
	Naphthylamine sulphonic	$NH_2C_{10}H_6SO_3H$ ...	α1 : 4				Naphthionic + $\frac{1}{2}H_2O$		106
	,, ...	$NH_2C_{10}H_6SO_3H$ ...	β1 : 4	C.c.			Na. salt w. 4aq.	VIII A, XIV, XVI	,,

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Group.	Name.	Formula.		Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
HYDROXY DERIVATIVES or PHENOLS.	Phenol	C_6H_5OH ...	...	C.c.	43	183		VI, IX B, XI, XV	125
	Cresols	$CH_3C_6H_4OH$	o	,,	31	188		,, ,, ,, ,,	,,
			m	L.c.	4	201			,,
			p	C.c.	36	198			,,
	Naphthols ...	$C_{10}H_7(OH)$ ...	α	,,	95	278		,, ,, ,, ,,	127
			β	,,	122	286	Benzoate [107]		,,
	Phenate Sodium...	C_6H_5ONa. ...	...	S.w.		D		as above	128
	Anisol	$C_6H_5OCH_3$ ...	...	L.c.	−38	152		VII B. then XI, etc.	129
	Phenetol	$C_6H_5OC_2H_5$ ...	...	,,	−34	172		,, ,,	,,
	Phenyl sulphuric acid	$C_6H_5OSO_2OH$	...	salts only				VII A, XI	—
	Phenyl Acetate ...	C_6H_5OAc. ...	...	L.c.	—	195	Carbonate [78]	,, ,,	129
	— Isocyanate	C_6H_5NCO ...	...	,,		163	Isothiocyanate L. (222)	VII A, XIV	—
	tri-Chlorphenol ...	$Cl_3C_6H_2OH$ ...	...	C.c.	68	244		VI, IX A	129
	— Brom — ...	$Br_3C_6H_2OH$ ...	...	,,	96		Sublimes	,, ,,	,,
	Nitrophenols ...	$NO_2C_6H_4OH$	o	C.y.	45	214	Salts w. metals	VI, IX A, XIV	130
			m	,,	96	194_{70}	,,		,,
			p	C.yw.	114	Not vol. in steam	,,		,,
	Picric Acid ...	$(NO_2)_3C_6H_2OH$	...	C.y.	122·5	D	Chlor [81-2]	VI, IX A	131
	Nitro-Naphthols	$NO_2C_{10}H_6OH$	α : 2	C.gr.y.	128			VI, IX A, XIV	130
			α : 4	C.y.	164				,,
			β : 1	,,	103				,,
	Amino-Phenols ...	$NH_2C_6H_4OH$	o	C.c.	170	D	Salts w. acids	VI, XIV, XV	133
			m	easily	122	D	,, ,,		,,
			p	colored	184 D		Sublimes ,,		,,
	Phenacetin ...	$AcNHC_6H_4OEt$	...	C.c.	135			VII A, etc.	,,
	Phenol Sulphonates ...	$HOC_6H_4SO_3H$	o	,,			Salts	XI, XVI	134
			m				,,		,,
			p	L.c.t.			,,		,,
	Naphthol Sulphonates ...	$HOC_{10}H_6SO_3H$	1 : 2	C.c.			,,		,,
			2 : 6	,,	122		,,	,, ,,	,,

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Group.	Name.	Formula.	Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
Polyhydroxy Derivatives.	Catechol ...	$C_6H_4(OH)_2$ ortho ...	C.c.	104	245	Carbonate [118](227) [Benzoate [84]	VIII C, XI	135
	Guaiacol ...	$C_6H_4 < {OH \atop OMe}$,, ...	,,	28	205	Me — veratrol [23](207)	XI	136
	Resorcinol ...	$C_6H_4(OH)_2$ meta ...	S.w.	118	276	Me_2(214)Ac_2(278) [Carbonate (300)	,,	135
	Quinol ...	$C_6H_4(OH)_2$ para ...	C.c.	169	285	Me_2 [56](205) Ac_2 [123]	VIII C, XI	,,
	Pyrogallol ...	$C_6H_3(OH)_3$ 1, 2, 3 ...	,,	132	293 D	Me_3 [47](235)	,, ,,	137
Quinones.	Benzoquinone	$C_6H_4O_2$ para ...	C.y.	116		Volatile in steam	IX A	138
	Chloranil ...	Mixture $C_6HCl_3O_2$ and $C_6Cl_4O_2$				,,		,,
	Toluquinone	$(CH_3)C_6H_3(O_2)$1:2:5	,,	67		,,	,,	,,
	α Naphtho —	$C_{10}H_6O_2$	,,	125	S	,,	,,	,,
	β — —		C.r.	115 D			,,	,,
	Anthra —	$C_{14}H_8O_2$	C.y.	277	378	Sublimes at 250°	,,	,,
	Phenanthra —	$C_{14}H_8O_2$	,,	202		Sublimes	,,	,,
Aliphatic-Aromatic Compounds.	Benzyl Alc....	$C_6H_5CH_2OH$ ...	L.c.o.		206		VIII A, X	140
	Saligenin ...	$C_6H_4 < {OH \atop CH_2OH}$ (1) (2)	C.c.	82		Sublimes at 100°	VIII B, XI	141
	Salicin ...	$C_{13}H_{18}O_7$	,,	201 dry			VII A and B, XI, etc.	,,
	Helicin ...	$C_{13}H_{16}O_7$	,,	175 dry		+ $\frac{3}{4}H_2O$	,, ,,	145
	Populin ...	$C_{13}H_{17}(C_7H_5O)O_7$ ...	,,	180		+ $2H_2O$	,, ,,	141
	Benzyl Chlor.	$C_6H_5CH_2Cl$	L.c.o.	−44	179		VII A, VIII B, IX A	142
	— Brom.	$C_6H_5CH_2Br$ ...	,,		210		,, ,, ,,	,,
	— Acetate	$C_6H_5CH_2OAc$ ...	,,		206		VII A, VIII B, XI	,,
	— Amine	$C_6H_5CH_2NH_2$ ...	,,		187		VIII A, XIV, XV	,,

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ALDEHYDES.	Benzaldehyde ...	C_6H_5HCO	L.c.o.	−13·5	179	Ph.Hydrazone[152]	VI, VIII A and D, XIII	143
	— oxime ...	C_6H_5HCNOH ...	C.c.	35	200	[C.y.		,,
	Amygdalin ...	$C_{20}H_{27}NO_{11}$... ...	S.w.	214	D		VII B, VIII D, XI, XIII	158
	Benzylidene Chlor	$C_6H_5CHCl_2$	L.c.	−16	206		VII B, IX A, XIII, etc.	145
	Hydrobenzamide	$(C_6H_5HC)_3N_2$ ...	C.c.	110				143
	Salicylaldehyde ...	$C_6H_4 < {OH \atop HCO}$ ...	L.c.o.	−20	196	becomes red	VIII A and D, XI, XIII	144
	m-HO-benzald. ...	,,	C.c.	104	240	,, ,,	,, ,, ,,	—
	p — — ...	,,	,,	116		Subl. become red		—
	Anisaldehyde ...	$C_6H_4(OMe)HCO$ p	,,	0	240			
	Phenylacetald. ...	$C_6H_5CH_2HCO$ ...	L.c.		206		VIII A, XIII	145
	Cinnamaldehyde	$C_6H_5CH:CH.HCO$	,,	−8	248 D		VIII A, XIII, XIX	—
KETONES.	Acetophenone ...	$C_6H_5COCH_3$ ...	L.c.o.	20	202	Ph. Hydrazone[105]	VIII A, XIII	145
	— oxime ...	$C_6H_5C(NOH)CH_3$ ...	C.c.	59			VII B, XIII	,,
	Benzophenone ...	$C_6H_5COC_6H_5$ ...	,,	46	305		VIII A, XIII	146
	— oxime ...	$C_6H_5C(NOH)C_6H_5$	,,	140			as above	,,
	Benzoin	$C_6H_5CHOHCOC_6H_5$	,,	137			VIII	—
	Benzil	$C_6H_5CO.COC_6H_5$ ...	C.y.	95	347		,,	—
	Camphor	$C_9H_{16}CO$	C.c.	175	209		VIII A, XIII?	

TABULAR INDEX.

Group.	Name.	Formula.		Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
AROM. ACIDS and Esters.	Benzoic ...	C_6H_5COOH		C.c.	120	250		X, XI	148
	Toluic ...	$CH_3C_6H_4COOH$	o	,,	102·5	259	Et (227) Amide [138]	,, ,,	,,
			m		110	263	,, (225) ,,		,,
			p		180	275	,, (228) ,, [151]		,,
	Benzoate Me	$C_6H_5COOCH_3$		L.c.o.		199		VII A, XIII A, X, XI	149
	,, Et	$C_6H_5COOC_2H_5$ ...		,,	−93	213		,, ,, ,, ,,	,,
	,, Ph	$C_6H_5COOC_6H_5$ ...		C.c.	+71	314		VII A, X, XI	,,
	,, Benzyl	$C_6H_5COOCH_2C_6H_5$ ...		L.c.		323		VII A, VIII A, X, XI	,,
DERIVATIVES OF AROM. ACIDS.	Benzoic Anhy.	$(C_6H_5CO)_2O$		C.c.	42	360		VI, X, XI	150
	Benzoyl Chlor.	C_6H_5COCl		L.c.t.	−1	198		,, ,, ,,	149
	Benzotrichlor.	$C_6H_5CCl_3$		,,	−22·5	213		VII, X, XI	,,
	Benzamide ...	$C_6H_5CONH_2$		C.c.	+128	290	Benzanilide [161] C.c.	VII, XI	150
	Hippuric ...	$C_6H_5CONHCH_2COOH$		,,	187	240 D	Et ester [60] C.c.	IV, VII B, XI	,,
	Benzonitrile	C_6H_5CN		L.c.	−17	191		VII A, XI	,,
	Tolylnitriles	$CH_3C_6H_4CN$ ...	o	,,		203		,, ,,	,,
			m	,,		213		,, ,,	,,
			p	C.c.	29	218		,, ,,	,,

TABULAR INDEX.

Group.	Name.	Formula.	Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
SUBSTITUTED AROMATIC ACIDS and their Derivatives.	Chlorbenzoic	ClC_6H_4COOH o	C.c.	137			IXA	151
		m	,,	153	Sublimes	M.-Brom [155]		,,
		p	,,	240				,,
	Nitrobenzoic	$NO_2C_6H_4COOH$ o	C.y.	147		Chloride Et ester [30]	IX A, XV	,,
		m	,,	141	Sublimes	[34] ,, [41]		,,
		p	,,	238	,,	[75] ,, [57]		,,
	Aminobenzoic	$NH_2C_6H_4COOH$ o	C.c.	145	D	Et ester (260)		,,
		m	,,	173				,,
		p	,,	186			XV	,,
	Anthranil ...	$C_6H_4 < {NH \atop CO}$ ...	C.c.	18	210 D			
	Sulphobenzoic	$C_6H_4 < {SO_3H \atop COOH}$ o	,,			+ 3aq Salts		152
		m	,,			+ 2aq ,,	XVI	
		p	,,			+ 3aq ,,		
	Saccharin...	$C_6H_4 < {SO_2 \atop CO} > NH$	C.w.	220				,,
	Salicylic ...	HOC_6H_4COOH ...	C.c.	155	D		X, XI	,,
	Salicy ate Me	$HOC_6H_4COOCH_3$	L.c.	−8·3	224		VII A, B, VIIIA, XI	153
	— Et	$HOC_6H_4COOC_2H_5$	,,	1·3	231·5		,, ,, ,,	,,
	— Ph	$HOC_6H_4COOC_6H_5$	C.c.	43	172_{12}	"Salol"	VII A and B, XI	154
	Acetosalicylic	$AcOC_6H_4COOH$...	,,	118	140 D	"Aspirin"	VII A and B	153
	p-HO-benzoic	HOC_6H_4COOH ...	,,	210 D		Me ester[131](270-80)		—
	Anisic ...	$MeOC_6H_4COOH$ p	,,	185	280	Et ,, [7](269)		154

TABULAR INDEX.

Group.	Name.	Formula.	Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
Dicarboxy Arom. Acids.	Gallic ...	$(HO)_3C_6H_2COOH$ aq 1:3:4:5	C.c.	220 D		Et ester [141] Ac_3 [ester 170 D]	XI	154
	Tannic ...	$C_{14}H_{10}O_9 + 2aq$ ...	,,	215 D			,,	155
	Phthalic Acid	$C_6H_4(COOH)_2$ ...	,,	195 D			X, XI	,,
	— Me	$C_6H_4(COOCH_3)_2$ ...	L.c.		280		II, VIII A, X, XI	,,
	— Et	$C_6H_4(COOC_2H_5)_2$ ...	,,		290 – 4		,, ,, ,,	,,
	Phth. Anhyd.	$C_6H_4 < {CO \atop CO} > O$ ...	C.c.	128	284		VI, X, XI	156
	PhthalylChlor.	$C_6H_4 < {CO \atop CCl_2} > O$ ...	L.c.o.	0	281		,, ,, ,,	155
	Phthalamic ...	$C_6H_4 < {CONH_2 \atop COOH}$ ...	C	148			IV, VII, XI	—
	Phthalimide	$C_6H_4 < {CO \atop CO} > NH$ ...	C.c.	233 – 5		Sublimes	VII, XI	157
Aliphatic Arom. Acids.	Phenylacetic	$C_6H_5CH_2COOH$ ...	,,	76	265	Nitrile(232)Me ester (218-20)	X	,,
	— propionic	$C_6H_5CH_2CH_2COOH$	,,	49	280	"Hydrocinnamic"	,,	158
	— glycollic	$C_6H_5HCOHCOOH$...	,,	118	D	"Mandelic." Me ester [52]	,,	,,
Unsat'd Acids.	Cinnamic acid	$C_6H_5HC:CHCOOH$	,,	133	300	Chlor. [35](154_{25})	VIII A, XI	,,
	Cinnamate Me	$C_6H_5HC:CHCOOMe$	,,	36	260		VII, VIII, XI	,,
	— Et	$C_6H_5HC:CHCOOEt$	L.c.	12	271	Ph ester[72](206)	,, ,, ,,	,,
	Coumarin...	$C_6H_4 \langle {CH:CH \atop O-CO}$ ...	C.c.	67	290	Acid $C_6H_4 < {CH:CHCOOH \atop OH}$ [208]		—

TABULAR INDEX.

Group.	Name.	Formula.	Form.	M.P. °	B.P. °	Remarks, etc.	Scheme.	Page.
ALKALOIDS.	Pyridine	C_5H_5N	L.c.	−42	113		VI, XVII	160
	Quinoline... ...	C_9H_7N	,,	−19·5	236	y. generally	,,	,,
	Morphine... ...	$C_{17}H_{19}NO_3$	C.c.	230	D	+ H_2O Salts	XI, XVII	165
	Cinchonine ...	$C_{19}H_{21}(OH)N_2$	,,	255	D		XVII	166
	Quinine	$C_{19}H_{20}(OCH_3)(OH)N_2$ ...		174	D		,,	165
	,, ...	,, + 3aq	,,	57	D			
	,, ...	,, + HCl or 2HCl ...			D			
	,, ...	,, + H_2SO_4 or $2H_2SO_4$			D			
	Strychnine ...	$C_{21}H_{22}N_2O_2$	,,	268	270_5	,,	,,	167
	Brucine	$C_{23}H_{26}N_2O_4$	,,	178	D	,,	,,	,,
	,, ...	,, + 4aq	,,	105	D			
	Cocaine (levo) ...	$C_{17}H_{21}NO_4$	,,	98	D	,,	,,	—
	Antipyrin... ...	$C_{11}H_{12}N_2O$		114	D	,,	XVIII?	—

APPENDIX III.

Melting Points.
Degrees Cent.
Boiling Points.
NH2COCl—Bromacetic ac.
50
Glyoxal
Cl3C.COOH—Me Urethane
Acrolein
Diphenylamine—
p-Nitrotoluene—
Me Oxalate
Et Formate
55
CH3COCl
Acetone
Quinine 3 aq.—Chloral Hydrate
Me Acetate
CH3CHCl2
Acetoxime
iso-Propyl brom.
60
Et isocyanate
β-brompropionic ac.
NH2COCl—Chloroform
Chloracetic ac.
m-Phenylenediamine
65
Cyanacetic ac.
MeOH—Me Nitrate
Trichlorphenol
70
Diphenyl—Ph. Benzoate
Propyl brom.—Allyl brom.
Crotonic ac.
EtI—Me Chlorcarbonate
75
Phenylacetic ac.
CCl4
Et Acetate
Et OH
Me Citrate—Naphthalene
Glycollic ac.
80
Propionyl chlor.
Ethylene Iod.
C6H6—Propyl Formate
Saligenin—Acetamide
CH3CN
iso-Propyl Alc.
C2H4Cl2
85
Dipropargyl
Glucose H2O
Et Nitrate
p-C6H4Br2
iso-Propyl Iod.
m-C6H4(NO2)2
90
iso-Propyl Acetate
Methyl Carbonate
Triphenylmethane
Valeraldehyde, iso.
Et Chlorcarbonate
Fructose—Benzil—α-Naphthol
95
iso-Amyl nitrite (96°)
Tribromphenol
Allyl alc.—Propylene Chlor.
Propyl alc.
Cocaine
Chloral and its Hydrate—Et Cyanide
Phenanthrene
Et Propionate
Malic—Citric. aq.
100
iso-Amyl Chlor.—Formic Acid
Water boils

Melting Points.
Degrees Cent.
Boiling Points.
100
Aldehydeammonia—Formin S.
Acetomethylaniline—Oxalic 2 aq.
Allyl Iod.—Nitromethane—Propyl [Acetate
Propyl Iod.
Diethyl Ketone
Catechol
Acetal—Crotonaldehyde
Brucine 4 aq.
105
CH2Cl COCl
β-Naphthyl Benzoate
iso-Butyl alc.
Hydrobenzamide]
—Sorbitol—o-Acetotoluide
110
Toluene—Ethylidene brom.
Pentacetylglucose
β-Naphthylamine : Acetanilide
to 115 Metaldehyde S.
Ethyl Oxamate : m-Nitraniline
Nitroethane—Pyridine
Antipyrin : p-Nitrophenol
β-Naphthoquinone D
115
Benzoquinone : Chloracetamide
Butyl alc.
p-hydroxybenzaldehyde :]
Resorcinol
Acetic ac.
Mannitol hexacetate : Tribromaniline
—Benzoic ac. : Iodoform
120
iso-Amyl brom.
Succinic anhydride :]
Me Crotonate
Picric ac. : β-Naphthol
Paracetaldehyde—Et Butyrate
α-Naphthoquinone
125
Butyl Acetate
Succinimide
Ethyl Carbonate
Benzidine—Triphenylamine
—Lactide : Phthalic anhydride
Benzamide :]
Active Amyl alc.
130
Ethylene dibrom.
Malonic ac. : Pyrogallol : Urea
iso-Amyl alc.
Cinnamic ac.
Phenyl Chlor.
Phenacetin
135
Acetoxime : Et iso-Valerate
Mannose
Benzoïn
Acetic Anhydride : n-Amyl alc.
p-Xylene
Acrylic ac. : m-Xylene
140
iso-Amyl Acetate
Propylene dibrom : Propionic ac.
Pentacetylgalactose
o-Xylene
Et Aminoacetate-HCl
Et Valerate : Et Chloracetate
Anthranilic ac.
145
Glucose
o-Nitrobenzoic ac.
iso-Amyl Iod.
Et Aminoacetate
Phenylsulphonamide
150
Oxalic S.

Melting Points.	*Degrees Cent.*	**Boiling Points.**
	150	
Thiocarbanilide		Bromoform—Allyl iso-Thiocyanate
		Anisol
p-Acetotoluide—Citric ac.		
		Et Lactate
Salicylic ac.	155	Phenyl Bromide—iso-Butyric acid
		Et di-Chloracetate
Sucrose	160	Et Glycollate
Paraformaldehyde		
Urea Nitrate		Butyric ac.: Methyl Oxalate: [p-Tolyl Chlor. iso-Valeric ac.
	165	
Mannitol		
d-Tartaric		
Galactose		Propionic Anhydride
Quinol		
	170	Amylene brom. to 180° D.
p-$C_6H_4(NO_2)_2$ (or 180°) Thiourea		Phenetol: Salol
Quinine		
	175	
		Me Urethane
Brucine		Ethylidene Iod.
		Benzaldehyde.—Benzyl Chloride
	180	Methylene Iod. D.—Crotonic ac.—[Me Malonate
		Et Acetoacetate
Succinic		Aniline
		Phenol
p-Aminophenol		Et Urethane
Anisic ac.	185	
		Chloracetic ac. (to 7): Et Oxalate: [Glycol di-Acetate
		Benzylamine
Hippuric ac.		Me_2SO_4—o-Cresol: Phenyl Iod. (or 190)
Oxalic ac.		
	190	Succinyl Chlor. (to 2)
		di-Chloracetic ac.—Benzonitril
$PhNH_3Cl$		iso-Amyl—iso-Valerate
		PhNHMe: $PhNMe_2$: Formamide D.
Mannose Phenylhydrazone	195	Trichloracetic ac.: Et Malonate (to 8) [Phenyl Acetate
		Salicylaldehyde
		o-Toluidine—Glycol
		p-Toluidine (or 200): p-Cresol: [Benzoyl Chlor.
		Me Benzoate
Lactosazone	200	

Melting Points.
Degrees Cent.
Boiling Points.
-200-
Salicin dry
Phenanthraquinone
Acetophenone
Et Aniline
Lactose
-205-
Galactosazone
Benzyl alc.
Nitrobenzene
Et_2SO_4 D: Bromacetic ac.
Glucosazone
Methylamine HCl
-210-
p-Tolyl Iod.
Et. Benzoate (or 13)
D. Phthalic ac.
o-Nitrophenol
-215-
Anthracene
Et Succinate
Naphthalene—o-Nitrotoluene
di-Brombenzene, p.
Gallic D.
-220-
Acetamide
Me Salicylate: Chloracetamide
-225-
Propylene Iod. D.
Morphine
-230-
Et Salicylate
Glycin
Caffein
-235-
Quinoline
p-Nitrotoluene
p-Nitrobenzoic ac.
-240-
Anisaldehyde—Hippuric D.
Phenyl Hydrazine
Trichlorphenol
-245-
Catechol
Cinnamaldehyde D.
-250-
Benzoic ac.

Melting Points.
Degrees Cent.
Boiling Points.
250
$PhSO_2Cl$ D.
Cinchonine
255
Lactide : Diphenyl
Glycerol Triacetate
260
Succinic Anhydr. CH_2Ph_2
265
Phenylacetic acid.
Strychnine
270
Et Cinnamate
275
Resorcinol
Anthraquinone
Me and Et Tartrates—Anisic ac.
α-Naphthol Hydrocinnamic acid
280
Et Citrate
Phthalic Anhydride—Formanilide
285
m-Nitraniline—β-Naphthol—Quinol
m-Phenylene Diamine
Benzamide—Et Phthalate
290
Glycerol
Pyrogallol D
295
β-Naphthylamine—Acetanilide
o-Acetotoluide
300
α-Naphthylamine—Cinnamic ac.

Melting Points.	*Degrees Cent.*	Boiling Points.
	300	
		m-di-Nitrobenzene
		Benzophenone
		p-Acetotoluide
	310	Diphenylamine
		Phenyl Benzoate
	320	
		Benzyl Benzoate
	330	
	340	Phenanthrene
		Benzil
		Triphenylamine
	350	
		Triphenylmethane 358°
	360	Benzoic Anhydr. } 360°
		Anthracine }
	370	
	380	Anthraquinone
	390	Benzidine
	400	

INDEX.

This Index contains the names of compounds referred to in Parts I. and II., but not given in the Tabular Index. Also it contains references to certain reactions and subjects not given in full in the Table of Contents.

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